



STUDIES ON MOLECULAR ASSOCIATION

A THESIS

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BY

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T4744

*TO
MY PARENT
FOR THEIR
IMMENSE LOVE & SACRIFICE*



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This is to certify that the Ph.D. Thesis
entitled "STUDIES ON MOLECULAR
ASSOCIATION", by Syed Muzaffar Ali
Andrabi is the original work of the
candidate and is suitable for
submission.

Pushkin M. Qureshi
Reader and Supervisor

S U M M A R Y

Molecular Association is a blanket cover for a wide variety of interactions. Truly, one can now say that molecular association lies somewhere on the reaction profile of every chemical reaction. In this study I have focussed my attention on Charge-Transfer Complexes, Hydrogen Bonding and Solvent Polarity Scales (based on charge-transfer complexes and certain aspects of Sigma Complexes which we have used in an Analytical study. Though Sigma Complexes are not exclusive charge-transfer complexes, nevertheless charge-transfer forces contribute significantly to this study. This thesis comprises of seven chapters. First is the General Introduction which is based on all the relevant literature to date.

The second chapter deals with the isolation of charge-transfer bands for various polynitroaromatics-aromatic amine systems). Even though efforts have been made, these bands could not be isolated before. The charge transfer has been confirmed independently by evaluating association constants. The electron affinities for some polynitroaromatics which are not known have been evaluated from their charge-transfer bands.)

It has not been possible to correlate the π^* -scale for solvent polarity with the $E_T(30)$, Z and AN scales etc. by a simple linear relation. To overcome this problem, the

α -scale was introduced for the hydrogen bond donor solvents. However, the many pitfalls in the way values were derived severely limited its utility. Therefore, in third chapter, a new solvent polarity scale $\bar{\phi}$ is derived which gives a linear relation with π^* and can be used without recourse to α , $\bar{\phi}$ is defined as

$$\bar{\phi} = \ln K$$

The estimated values of $\bar{\phi}$ are based on the evaluation of equilibrium constants for the 2,4-dinitrotoluene-diphenylamine charge-transfer complex in different strong and weak hydrogen bond donor solvents.

Nitromethane has been a centre of controversy in its molecular complexes. Usually it is difficult to distinguish whether there is charge-transfer or hydrogen bonding in several of its complexes. In fourth chapter I have given convincing evidence that both the interactions are simultaneously involved. This has been established by using both electronic and NMR spectrometry.

Studies on molecular complexes of organometallic donors and acceptors is of very recent origin. Though alkyl donors have been extensively studied, very few studies have appeared on aryl donors. Fifth chapter deals with a study on the charge-transfer complex between triphenylantimony and 1-chloro-2,4-dinitrobenzene. An interesting feature of

this study is that two charge-transfer bands are observed. IR studies confirm the molecular complexation in this system. Equilibrium constant has been measured.

A major problem in the evaluation of association constants for molecular complexes by graphical methods based on the Benesi-Hildebrand equation is that a separation of terms in $K \epsilon$ is required. Which leads to significant errors. Therefore, in sixth chapter a new equation is proposed for UV-visible and NMR both. The equations take the form:

$$\text{UV-visible: } \frac{1}{[D]_0} = \frac{K \epsilon [A]_0}{A} - K$$

$$\text{NMR: } \frac{1}{[D]_0} = \frac{\Delta_0 K}{\Delta} - K$$

By using above equations K may be evaluated directly without separation of K ; though evaluation of ϵ will require a separation of the terms. However, K is usually the desired parameter and since ϵ is comparatively very large the errors involved in the evaluation of ϵ will be small.

The final chapter deals with an analytical method for the analysis of 2,4-dinitrophenylhydrozone involving an anionic Sigma complex and a hydrogen bonded species. Since charge-transfer forces contribute to the stability of both

the sigma complex and the hydrogen bonded species, the reaction is the one involving molecular association in its mechanism. Since most colorimetric methods for polynitroaromatics are handicapped a kinetic method has been developed for the analysis of 2,4-dinitrophenylhydrazine which is an important pharmaceutical. 2,4-dinitrohydrazine is also an important reagent for a variety of functional groups and especially for the carbonyl group. It gives a green colour with piperidine in DMSO which is the basis of this kinetic method. Other aliphatic amines too give a green colour but the kinetic behaviour with piperidine is exclusive and distinguishing.

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LIST OF PUBLICATIONS

1. Charge-transfer bands of polynitroaromatics-diphenylamine system.
Spectrochim. Acta (In Press)
(Pergamon Press, U.K.).
2. Kinetic method of analysis for an important pharmaceutical 2,4-dinitrophenylhydrazine.
Analytical Proceedings (In Press)
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CHAPTER - 1

GENERAL INTERODUCTION

Molecular association is a blanket term which includes all those interactions where no chemical bonds are formed. They extend from hydrogen bonding to proton transfer reactions and include the most important of this family of interactions namely charge-transfer complexes or molecular complexes, including solvent polarity scales based on them. These complexes are becoming increasingly important in all fields of human endeavour from physics to chemistry and biology to medicine. Currently there is an opinion among some scientists that these complexes are involved somewhere or the other on the reaction profile of all chemical reactions. These are a special case of molecular association and have been most widely investigated.

1.1 THE THEORY OF CHARGE TRANSFER COMPLEXES

It has been known for a long time that hydrocarbons such as naphthalene react with picric acid to form a coloured substance. The nature of these coloured substances has only been recently understood. Briegleb^{1,2} suggested that the hydrocarbon-nitro compound adducts were the result of the electrostatic attraction between the localized dipoles of the nitro groups and the induced dipoles in the hydrocarbons. This theory could explain the bonding energy of a few kilocalories per mole which had been observed. However, the formation of colour could not be explained by this theory. Pauling³ suggested that when a hydrocarbon

molecule is close to picric acid (at a distance of a 3.5 \AA) and also parallel to it then the dielectric constant of the environment of the picric acid molecule is affected. This effect results in greater optical absorption. The distance between the component molecules in a complex was shown by crystallographic measurements to be only slightly less than the van der Waal's distance⁴⁻⁷. This observation finally removed the possibility that any sort of normal covalent bonding could be responsible for these complexes. On theoretical considerations too, the instant equilibrium in solution disfavors covalent bonding.

In 1949 Benesi and Hildebrand⁸ reported that solutions containing an aromatic hydrocarbon and iodine had an electronic absorption band not present in either component alone. In 1950 Mulliken⁹ suggested that complex formation occurs through an intermolecular charge-transfer transition. The detailed theory was put forward by him in 1952^{10,11}. As a result of Mulliken's theory there has been a great stimulus to the developments in the study of the charge-transfer (CT) complexes. A brief outline of his theory is presented here.

Mulliken's Theory

Mulliken defines a molecular complex between two molecules as an association somewhat stronger than ordinary

van der Waal's association, of definite stoichiometry (1:1 for most cases). The partners are very often already closed-shell (saturated valence) electronic structures. In loose complexes the identities of the original molecules are to a large extent preserved. The tendency to form complexes occurs when one partner is an electron acceptor and the other is an electron donor. We abbreviate the term donor-acceptor complex to include all such associations and use D for an electron donor and A for electron acceptor. Most studies of complexes thus far have been made in solution, in solvents that are as inert as possible. We may, therefore, assume that the London dispersion interactions which are important between D and A in the vapour state, are very approximately cancelled by losses of solute-solvent dispersion force attractions when complex is formed from free donor and acceptor in solution. Roughly one donor-solvent plus one acceptor-solvent contact is replaced by one donor-acceptor and one solvent-solvent contact. The theory of donor-acceptor complexes and their spectra as presented by Mulliken is a vapour-state theory, except for the omission of the London dispersion attraction terms. This theory after small correction for solvation energies is essentially valid for solutions in inert solvents. The few studies that have been made on vapour-state complexes are in general agreement with this theory but they show some puzzling features.

The new band found by Benesi and Hildebrand is in the ultra-violet region for a solution of benzene and iodine dissolved in n-heptane. Similar bands also occur in the visible region for many other complexes. To demonstrate this a solution of tetracyanoethylene (TCNE) in methylene dichloride may be added to a series of aromatic hydrocarbons dissolved in methylene dichloride. Benzene gives a yellow solution, xylene an orange, durene a deep red and hexamethylbenzene a deep purple. The π -electron molecules, ethylene and benzene can act either as weak donors or weak acceptors. Other things being equal, donor ability increases with decreasing ionization potential (I^D); the acceptor ability with increasing electron affinity (E^A). Among aromatic hydrocarbons I^D decreases and E^A increases with increasing size; graphite with $I^D = E^A$ is the extreme example and is in fact both a good acceptor and a good donor. Starting with any unsaturated or aromatic hydrocarbon, either its donor or its acceptor capability can be strengthened by the introduction of suitable substituent groups. The weak donor properties of benzene is fortified by adding more and more electron-releasing methyl groups (inductive effect) whereas the increase of nitro groups greatly fortifies the acceptor capability of benzene. The two kinds of molecular complexes discussed above provide examples of n.v. (strong) and of π - π^* (weak) complexes. The common types of donors and acceptors are listed in Table-1

TABLE 1
COMMON TYPES OF DONORS AND ACCEPTORS

Donor type	Example	Dative electron ^a from	Acceptor type	Example	Dative electron goes to
n	:NR ₃	Non-bonding lone pair	v	BCl ₃	Vacant orbital
b π	Benzene	Bonding π orbital	a π	TCNE	Antibonding π -orbital
			a σ	I ₂ , HQ ^b	Antibonding σ -orbital

a. "Dative electron" refers to the electron transferred from donor to acceptor.

b. Molecules such as phenol, water, and other molecules that give hydrogen bonding.

G.N. Lewis¹² explained coordination compounds or dative compounds (e.g., $R_3N:BCl_3$ which can also be considered as an essentially stable molecular complex) in terms of a structure with sharing of the electron lone pair of the nitrogen atom between the N and B atoms. By this sharing the N atom as well as the B atom are surrounded by a complete octet of outer-shell electrons. This sharing can be expressed in quantum-theory language by an approximate wave function Ψ that is a combination of two resonance structures (D here is R_3N , A is BCl_3):

$$\Psi_N(AD) \approx \underset{\text{no-bond}}{a \Psi_0(A,D)} + \underset{\text{dative}}{b \Psi_0(A^- - D^+)} \dots (1)$$

The dative structure corresponds to an ionic plus a covalent bond and has sometimes been called a semipolar double bond. The interpretation of the N-B dative bond in the complex as given by (1) is analogous to the approximate ionic covalent resonance interpretation of the chemical bond in HCl:

$$\Psi_{(HCl)} \approx \underset{\text{ionic}}{a \Psi_0(H^+, Cl^-)} + \underset{\text{covalent}}{b \Psi_1(H - Cl)} \dots (2)$$

In both examples $b \gg a$. The inclusion of the no bond structure in (1) is even more important than that of the ionic structure in (2).

Complexes are classified as strong or weak depending on whether the energy of formation and the equilibrium

constant (K) are large or small. Increasingly strong donors and/or acceptors form increasingly stable complexes.



Equation (1) shows that the complex is stabilized by resonance between ψ_0 and ψ_1 . The forces involved being called Charge - Transfer (CT) forces. However, classical electrostatic forces (including induction forces) also contribute to the stability of the complexes and may even be of predominant importance for the stability of the most hydrogen bonded complexes and of the weaker of the complexes of the $b.\pi - a.\sigma$ and the benzene-iodine ($b.\pi - a.\sigma$) type¹³.

In terms of the resonance structure description of (1) the structure of the ground state of any 1:1 complex is

$$\psi_N = a \psi_0 (A,D) + b \psi_1 (A^- - D^+)$$

This function is normalized as follows:

$$\int \psi_N \psi_N d\tau = \int a^2 \psi_0^2 d\tau + \int b^2 \psi_1^2 d\tau + \int 2ab \psi_0 \psi_1 d\tau \dots (3)$$

Since ψ_N, ψ_0 and ψ_1 are all normalized hence

$$\int \psi_N^2 d\tau = 1, \int \psi_0^2 d\tau = 1 \text{ and } \int \psi_1^2 d\tau = 1$$

Substituting these values in equation (3) we obtain

$$a^2 + 2ab \int \psi_0 \psi_1 d\tau + b^2 = 1 \dots (4)$$

$\int \psi_0 \psi_1 d\tau$ is called the overlap integral and is represented by S_{01} with the integration carried over all space. If the complex is loose S_{01} is small and

$$a^2 + b^2 \simeq 1 \quad \dots (5)$$

Here b^2 approximately measures the weight of the dative structure or the fraction of an electron transferred from the donor to the acceptor in the ground state. The term $2abS_{01}$ can easily be as large as b^2 or larger. Half of this term can reasonably be assigned to the donor and half to the acceptor so that the fractions F_0 and F_1 in the no-bond and dative structures are:

$$F_0 = a^2 + abS_{01}, F_1 = b^2 + abS_{01} \quad \dots (6)$$

In loose complexes between closed-shell donors and acceptors $b^2 \ll a^2$. For benzene. I_2 , b^2 is perhaps 0.06 or less; for pyridine. I_2 , b^2 is approximately 0.2; for trimethylamine. I_2 , b^2 may be 0.4.

If the ground state structure of the complex (weak or strong) is given by ψ_N then according to quantum theory principles there must be an excited state ψ_E where ψ_E refers to the CT state. ψ_E is given by

$$\psi_E (AD) = a^* \psi_1 (A^- - D^+) - b^* \psi_0 (A, D) \quad \dots (7)$$

The coefficient a^* and b^* are determined by the quantum theory requirement that the excited-state wave function be orthogonal to the ground state function i.e. $\int \psi_N \psi_E d\tau = 0$. The excited state function ψ_E is normalized as follows:

$$\Psi_E^2 d\tau = a^{*2} + b^{*2} - 2a^* b^* S_{01} = 1 \quad \dots (8)$$

This makes $a^* \simeq a$ and $b^* \simeq b$. If S_{01} were zero, $a = a^*$ and $b = b^*$ would be true exactly.

For loose molecular complexes the ground state is mostly no-bond that is, $a^2 \gg b^2$. According to the orthogonality requirements the excited state is mostly dative i.e. $a^{*2} \gg b^{*2}$. The excitation of an electron from Ψ_N to Ψ_E essentially amounts to the transfer of an electron from D to A. The theory further shows that spectroscopic absorption from Ψ_N to Ψ_E should occur with generally high intensity.

Complexes have been studied mostly in solution but some studies have been made in solids¹⁴⁻²⁶ and in the case of n.v. compounds and also recently of a few complexes of weaker types in the vapour state^{27,28}. Complexes in solids even when of 1:1 stoichiometry do not always occur in the form of pairwise units. Studies in the vapour state are difficult because K is small and interference of overlapping spectra of the uncomplexed components is often severe. These difficulties are also found for solution studies but they are less troublesome because K is larger. The complete absorption spectrum of a complex consists of absorption due to the following:

- (1) Locally excited states (states of A or of D, more or less but usually not greatly modified in the complex).
- (2) CT states [Ψ_E , as in (7) and other CT states involving excited dative structures, for example $\Psi_{(D^{+*} - A^-)}$, $\Psi_{(D^+ - A^{-*})}$].

Figure 1 shows the change that occurs in the spectrum of iodine when it dissolves in n-heptane and then when ethanol is added (ethanol is transparent upto 220 nm). The peak of the $C_2H_5OH \cdot I_2$ CT band is marked in the figure, and the position of the shifted visible absorption band of I_2 in the complex (a transition to a locally excited state) is also indicated. The contact CT band appears as a long wavelength shoulder on the ultra-violet iodine band when I_2 is dissolved in heptane. It is felt by some authors that the importance of CT forces in stabilizing the ground state of such complexes has been exaggerated.

Dewar's Theory

Mulliken's theory is a valence bond approximation in which the complex formed by a donor D and an acceptor A is represented as a resonance hybrid of the uncharged aggregate (a) and the ionic structure (b) formed from it by transfer of an electron from D to A. The appearance of a new band in

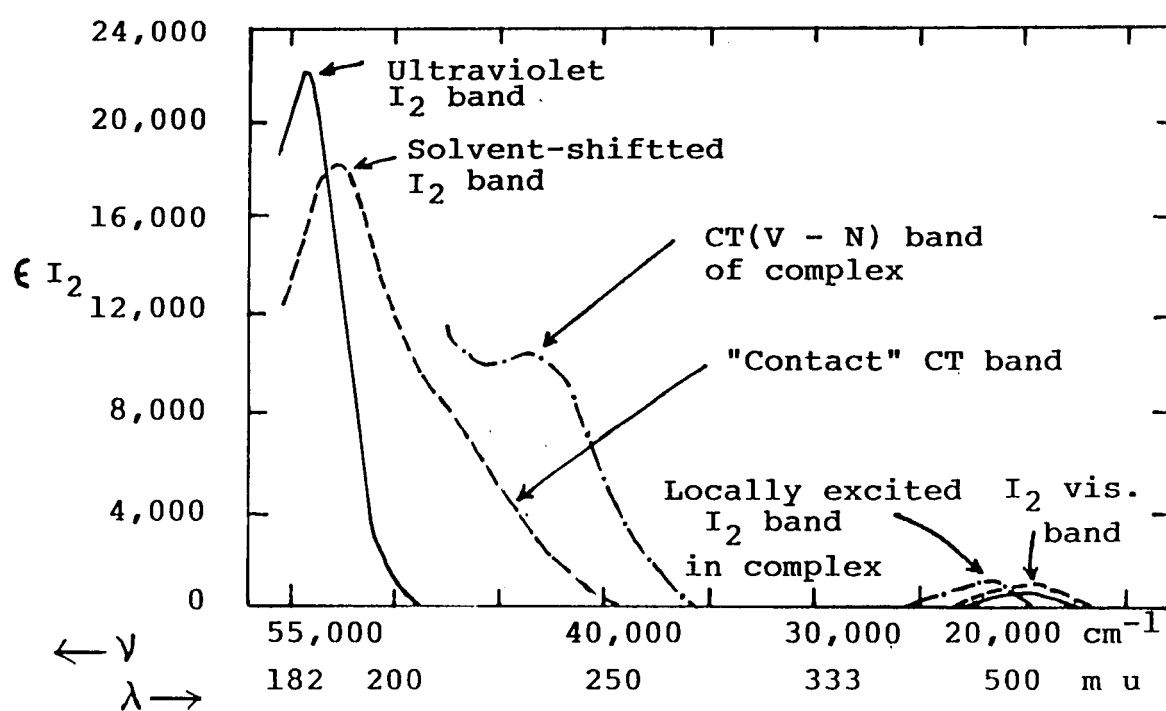


Fig. 1 The apparent molar absorptivity of I_2 vapor and of I_2 and EtOH. I_2 in n-heptane, Here — is for I_2 vapor, --- for I_2 in n-heptane, and -.-.- for I_2 in n-heptane with 3.4 M ethyl alcohol.

the spectrum of such a complex is ascribed to a transition from the ground state which is mostly (a) mixed with a little (b) to an excited state which is mostly (b) mixed with a little (a). This transition is of CT type and the complexes have accordingly been termed CT complexes.



This problem has been approached in terms of molecular orbital treatment by Dewar and Lepley²⁸. The essential features of this treatment are presented below.

The complex DA is represented as a π -complex formed by the interactions of the π -orbitals of D and A. As the interaction is small it may be treated by the perturbation theory²⁹. Consider the orbitals of D and A (Figure 2). Interactions between the filled bonding orbitals of D and A lead to no change in their total energy and there is no net transfer of charge between D and A. Interactions of the filled orbitals of D with the empty antibonding orbitals of A depress the former and raise the latter leading to a net stabilization with a simultaneous transfer of negative charge from D to A; interactions of the filled orbitals of A with the empty orbitals of D also lead to stabilization with a net charge-transfer in the opposite direction. These interactions are inversely proportional to the difference in

energy between the interacting orbitals. In complexes of this kind one component is normally a molecule of donor type (i.e., with filled orbitals of relatively high energy), the other an acceptor (i.e., with empty orbitals of relatively low energy); the main interaction is therefore between the filled orbitals of the donor and the empty orbitals of the acceptor, as indicated in Figure 2; this leads to a net transfer of negative charge from the donor D to the acceptor A.

The heats of formation of complexes of this kind are at least an order of magnitude less than their lowest transition energies; this suggests that the changes in energy of the orbitals in forming the complex are small compared with the spacing between the filled (bonding) and empty (antibonding) orbitals. The energies of the orbitals in the complex should, therefore, be little different from those in the separate components. All the possible transitions observed in D and A should, therefore, appear in the spectrum of DA, and this is commonly the case. Transitions of this type are described as locally excited³⁰. There should also be CT transitions of electrons from a filled orbital of D into an empty orbital of A and from a filled orbital of A into an empty orbital of D. Figure 2 indicates that transitions of the former kind may occur at lower energies than the locally excited transitions and so

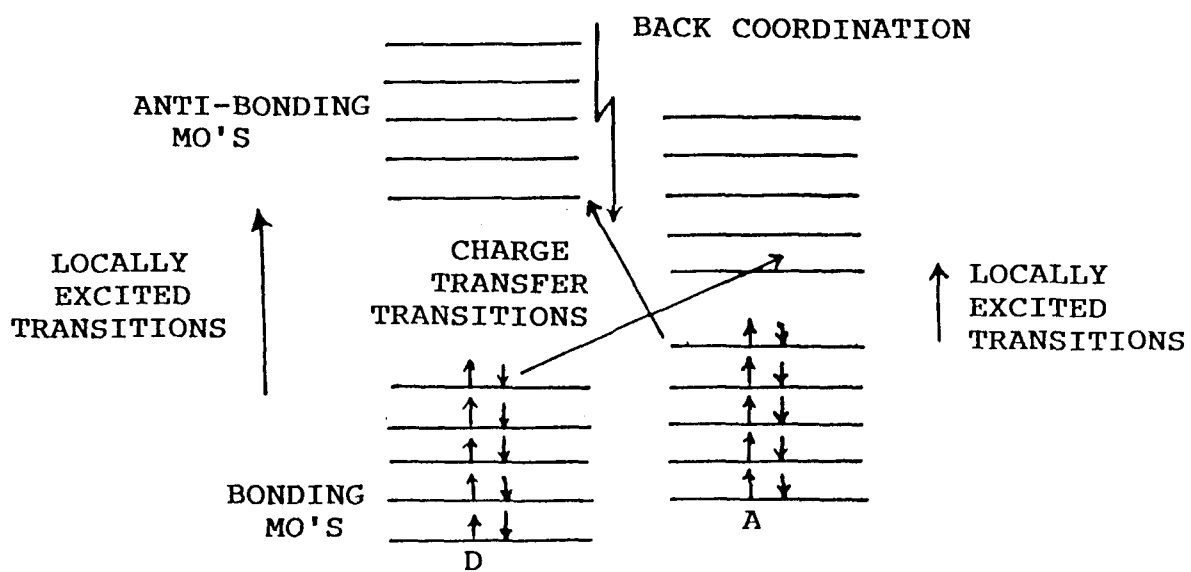


Fig. 2 Orbital energies and transitions in a molecular complex formed by a donor D and acceptor A.

lead to the appearance of new absorption bands at lower frequencies. This explains the new bands commonly observed in the spectra of such complexes which are responsible for their colour.

This treatment leads to conclusions similar to those given by the valence bond approach, but it seems preferable for two reasons. First there are cases when more than one new CT band appears in the complex DA; this can be explained in terms of the molecular orbital approach as there should be bands corresponding to transitions between any of the occupied orbitals of D and empty orbitals of A. Secondly the term "charge-transfer complex" is misleading in that very little charge is transferred in the ground states of such complexes and in that an appreciable part of their stability may be due to back coordination involving interactions between the filled orbitals of the acceptor and the empty orbitals of the donor. The term " π -complex" seems preferable for compounds of this type. If the interactions between donor and acceptor are small, the transition energy ΔE_0 for the first CT band should by either treatment be given by

$$\Delta E_0 = I^D - E^A + \text{constant} \quad \dots (9)$$

where I^D is the ionization potential of D (equal to the energy of the highest occupied molecular orbital in a simple

molecular orbital approach) and E^A is the electron affinity of A (likewise equal to the energy of its lowest unoccupied orbital). If then the acceptor is kept constant, ΔE_0 should vary linearly with the ionization potential of the donor; this relation has been observed in a number of cases³¹. In the molecular orbital approach, equation (9) is replaced by the more general equation

$$\Delta E_{ij} = D_i - A_j + \text{constant} \quad \dots (10)$$

where ΔE_{ij} is the transition energy for the CT band involving the filled orbital i of D (energy D_i) and the empty orbital j of A (energy A_j). This is equivalent to equation (9) in the case of first CT band, for the ionization potential of the donor should be equal to the energy of its highest occupied molecular orbital. If equation (10) is valid the energies of the CT transitions should be predictable from simple molecular orbital theory. Thus the energies of the first CT transitions of a variety of donors with a given acceptor should be a linear function of the energies of the highest occupied orbitals of the donors.

1.2 MULTIPLE CHARGE-TRANSFER SPECTRA

We can see from Table 2 that the intensity of CT spectra of the iodine-benzene complex is very large and that

both the K value and the value of $-\Delta H$ increase proportionately with increasing size of electron donor hydrocarbons. However, the intensity of the CT spectra is inversely proportionate with increasing donor size. In particular, CT spectral intensity of the anthracene-iodine complex seems to be weaker than that expected from the assumption that the CT spectra may borrow much of their intensity from strong absorption bands of the donor itself. This assumption is valid because these catacondensed hydrocarbons have several lower excited states allowed strongly from the selection rule. In connection with this problem Murrell³² proposed the following discussion. Generally the MO's of aromatic hydrocarbons spread over the whole molecule so that the overlap between the electron donor orbital and the accepting (σ , u of the I_2 molecule) orbital becomes smaller for large hydrocarbons than for smaller ones. As a result, the CT intensity of the iodine complexes with large hydrocarbons results in a weaker intensity compared with that of the complexes with small size hydrocarbons. At the same time the stability of the complexes should decrease with increasing donor size of hydrocarbons as CT theory suggests. Actually, however, K and $-\Delta H$ values turn out to be larger with increasing size of hydrocarbons, i.e., complexes become stable, as Table-2 shows.

TABLE 2
SPECTROSCOPIC AND THERMODYNAMIC DATA OF IONIC COMPLEXES
WITH SOME AROMATIC HYDROCARBONS

Donor	K (Temp.) solv	ϵ_{CT} ($\lambda_{CT_{max}}$) (solv)	H (solv) K cal mole ⁻¹
Benzene	0.15(25°C) ^a CCl ₄	16.400(292 mμ) (CCl ₄) ^a	-1.3(Hexane) ^b (CCl ₄) ^c
Naphthalene	0.25(25°C) ^a CCl ₄	7.150(360 mμ) (hexane) ^b	-1.8(Hexane) ^b
Phenan- therene	0.45(23°C) ^d CCl ₄	7.100(364 mμ) (CCl ₄) ^d	--
Anthracene	3.0(23°C) ^d CH ₂ Cl ₂ , CCl ₄	~ 550 at 430 mμ (430 mμ) (CCl ₄) ^d	-1.6(CCl ₄) ^d

a. L.J. Andrews and R.M. Keefer; J. Am. Chem. Soc., **74**, 4500 (1952).

b. J.A.A. Ketelaar; J. Phys. Rad., **15**, 197 (1954).

c. R.M. Keefer and L.J. Andrews; J. Am. Chem. Soc., **77**, 2164 (1955).

d. J. Peters and W.B. Person; J. Am. Chem. Soc., **86**, 10 (1964).

The main reason for these results may be as follows: When hydrocarbons increase in size there appear many MO's whose energies are not so well separated from one another. Hence it is possible that the charge-transfer is also brought about from deeper MO's as well as the highest occupied MO of hydrocarbons. Thus these CT states can interact with the ground non-bonding state, resulting in greater stabilization of the ground state. As a net result the complex becomes more stable as the ring size of hydrocarbon becomes larger. The CT bands caused by the charge-transfer from deeper donor orbitals will be hidden under the absorption bands caused by the donors or acceptors themselves.

Multiple CT bands, especially two CT bands, have been reported by many workers for various kinds of molecular complexes. A typical example is shown in Figure 3³³.

1.3 U.V.-VISIBLE SPECTRA

In general a complex formed between an electron donor and an electron acceptor still retains the absorptions of the components modified to a greater or lesser extent, together with one or more absorption bands characteristic of the complex as a whole. The recognition of this fact by Brackman³⁴ was important historically because it led to the realization that the absorption is the result of an

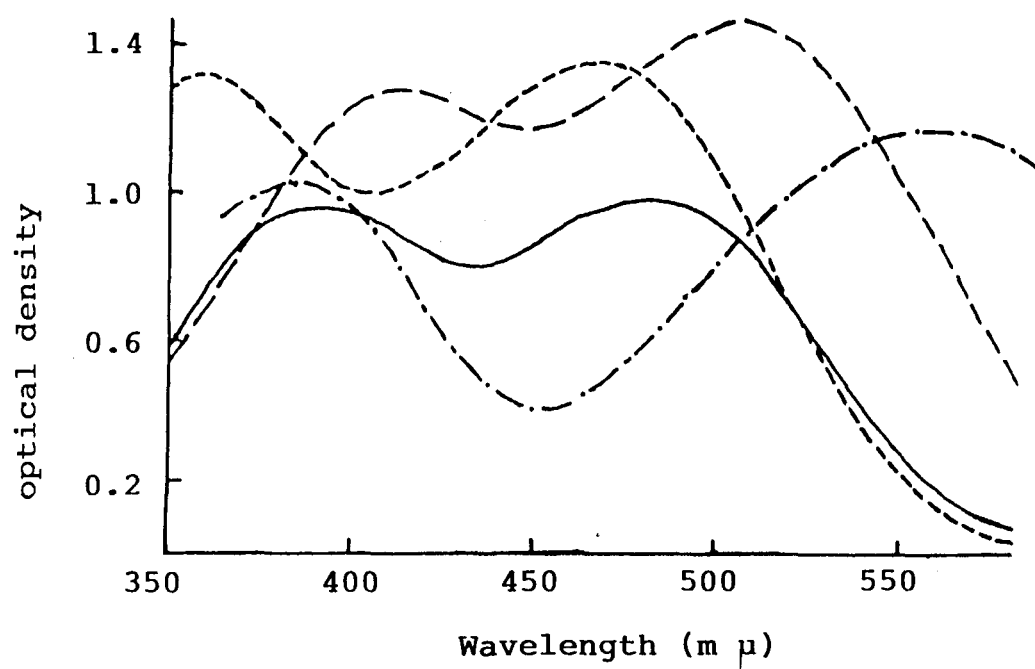


Fig. 3 Two CT absorption spectra observed on the chloranil-substituted naphthalene π - π complexes in CCl_4 ; — naphthalene, --- α -chloronaphthalene — α -methylnaphthalene -.-.- α -methoxynaphthalene. [Reproduced from A. Kuboyama; J. Chem. Soc. Japan, 83, 376 (1962)].

intermolecular charge-transfer transition and not a modified transition of one or other component.

In practice the absorption characteristic of the complex in solution may not be easily observed since the complex will be partially dissociated into its component species. It may be particularly difficult to measure those absorption bands due to "local excitation", when the interaction is between strong donor and strong acceptor. In such cases the transition usually appears as a separate band considerably at longer wavelengths than the absorption of the component molecules. The intensity of absorption band of a complex is usually determined as the molar absorptivity (extinction coefficient) at the wavelength of maximum absorption. A direct determination of intensity cannot normally be made because the degree of dissociation of the complex in solution is usually significant. Solid charge-transfer complexes have been studied by transmission³⁵⁻⁵⁵ and reflection⁵⁶⁻⁵⁸ spectra using specular reflection from a single crystal⁵⁸. Soon after the publication of Mulliken's charge-transfer theory, Nakamoto³⁵ provided an experimental observation which could be well explained in terms of this theory, whereas the absorption of polarized light by oriented crystals and of pure aromatics shows a stronger low energy absorption when the electric vector is parallel than when it is perpendicular to the ring, the opposite obtains

for the lowest energy intermolecular charge - transfer transition of a complex between the two planar molecules (Figure 4).

If a number of donors are complexed with a single acceptor, a refined parabolic relationship of the form in equation (11) follows

$$h \nu_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \quad \dots (11)$$

where C_1 and C_2 are constants for a given acceptor. This equation best correlated the data available then. As the range of donors is increased, some changes in these values can be expected. Slightly prior to the application of equation (11) McConnell et al⁵⁹ showed that there is an approximate linear relationship between I^D and ν_{CT} for complexes of iodine with the wide range of relatively weak donors.

$$h \nu_{CT} = I^D - E^A - W \quad \dots (12)$$

where E^A is electron affinity of the acceptor and W is dissociation energy of the charge-transfer excited state. Since the publication of that paper, similar linear relationships have been described for complexes of many other acceptors. In general

$$h \nu_{CT} = a I^D + b \quad \dots (13)$$

when there is linear correlation between I^D and $h \nu_{CT}$, it

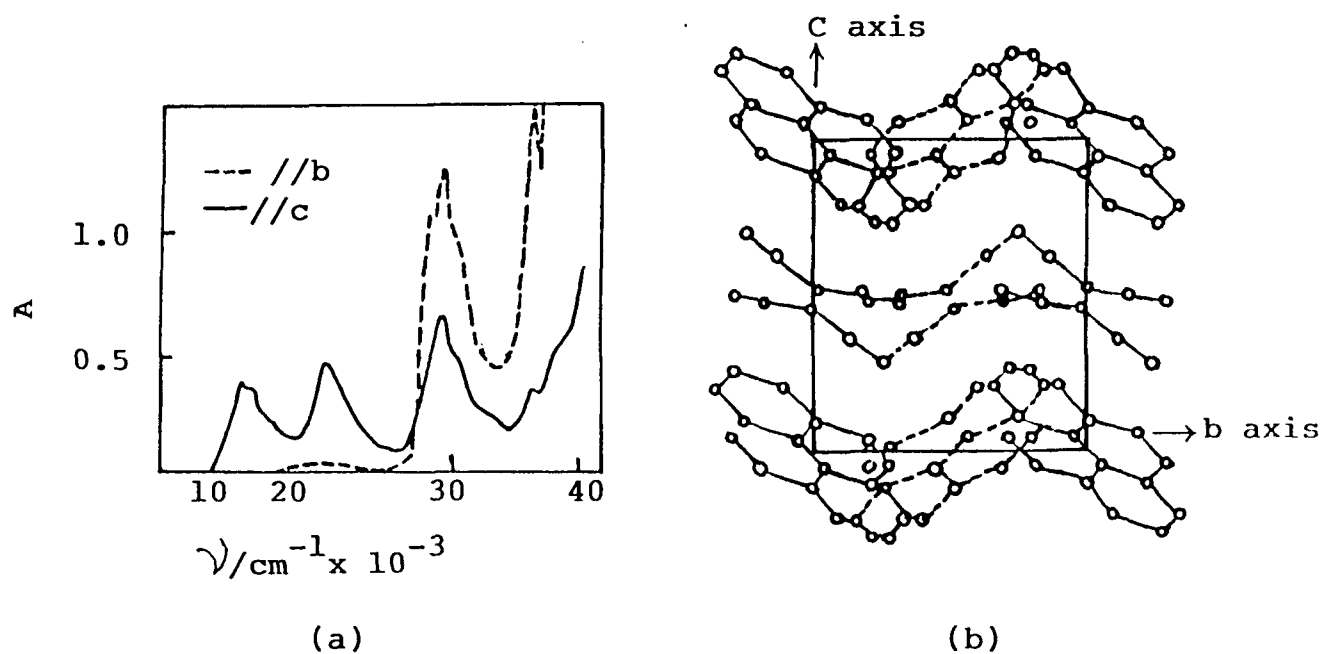


Fig. 4 The solid complex pyrene-tetracyanoethylene: (a) the polarized absorption spectra of a single crystal: (b) a projection of the crystal structure along the a-axis on the bc plane showing the orientation of the b- and c-axes.

is taken as a confirmation of a charge-transfer complex, though there is no theoretical justification. There is a similar linear relationship between the electron affinity of series of acceptors, complexed with a single donor and $h\nu_{CT}$ of the type

$$h\nu_{CT} = a E^A + b \quad \dots (14)$$

The electron affinity of a number of acceptors has been evaluated from polarographic half wave potential by the equation

$$E^A = - E_{\frac{1}{2}}^{red} + 1.41 \quad \dots (15)$$

The energy of charge-transfer band is correlated with the Huckel coefficients as follows

$$h\nu_{CT}(A_1) - h\nu_{CT}(A_2) = B_j(A_1) - B_j(A_2) \quad \dots (16)$$

Kosower⁶⁰⁻⁶³ has shown that ν_{CT} for the complex between the iodide ion and a pyridinium ion is extremely solvent sensitive. For complexes in which the components are oppositely charged species, the ground state may be expressed as predominantly an ion pair with a small admixture of a structure involving a pyridinium radical and an iodine atom with the two odd electrons coupled, i.e. $a^2 \ll b^2$ in equation (1), in contrast to the ground state of a weak complex formed of two neutral species where $a^2 \gg b^2$. The excited state of the pyridinium complex will be given by equation (1)

$$\psi_E = a^{\#} \psi_0 (A, D) - b^{\#} \psi_1 (A^- - D^+) \quad \dots (17)$$

where $a^{\#2} \gg b^{\#2}$.

1.4 I.R. SPECTROSCOPY

The CT studies in the solids and in solution state very clearly focus our attention on the differences in the two approaches. Thus infra-red measurements provide no information about relative orientation of the donor and acceptor in the complex solution. Infra-red spectrum of the solid bromine - benzene complex⁶⁴ has enabled some modifications to be made to the crystal structure description determined by X-ray diffraction. The infra-red spectrum which includes a bromine-bromine stretching vibration is inconsistent with the crystal structure⁶⁵ having an axial configuration with chains of alternating benzene and halogen molecules, in which the halogens are equidistant from two neighbouring benzene molecules in the chain and are centres of symmetry. Person et al⁶⁹ suggest that these conflicting observations can be reconciled if, in the crystals the halogen molecules are not, in fact, exactly equidistant from their immediate benzene neighbours in the chain, but are somewhat closer to one than the other.

The solid state studies on the tetracyanoethylene (TCNE) and hexamethylbenzene (HMB) system has been very rewarding. Two complexes with a mole ratio of 1:1 & 1:2 have

been prepared^{66,67}. The infra-red spectra of the two complexes are given in Figure 5. The spectra of the 1:2 complex may be interpreted in terms of a structure which consists of stacks which contain sequences of D.A.D. D.A.D. D.A.D. molecules. In the 1:1 complex the out-of-plane infra-red spectrum shows no absorption at 1295 cm^{-1} (an absorption assigned to the totally asymmetric C-CH₃ stretching mode of HMB which is forbidden in the free molecule). This is to be expected in terms of Ferguson and Matsen's⁶⁸⁻⁷⁰ and Person and Friedrich's⁷¹ theory since the charge oscillation between D and A, characteristic of a vibronic interaction, is effectively zero in symmetrical D.A. D.A. D.A. sequence of the 1:1 complex. However, in the 2:1 complex, the lower symmetry of the environment of the donor molecules permits the charge oscillation, and a strong absorption is observed at 1295 cm^{-1} . By contrast, the symmetry of environment of the TCNE molecule should be comparable in the 1:1 and 1:2 complexes. The similar absorption of the totally symmetric double bond mode of TCNE at 1560 cm^{-1} in the two complexes provides support for this conclusion.

The acceptors are generally classified as non acidic and acidic compounds. The former type can only form DA complexes involving electron transfer while the acidic

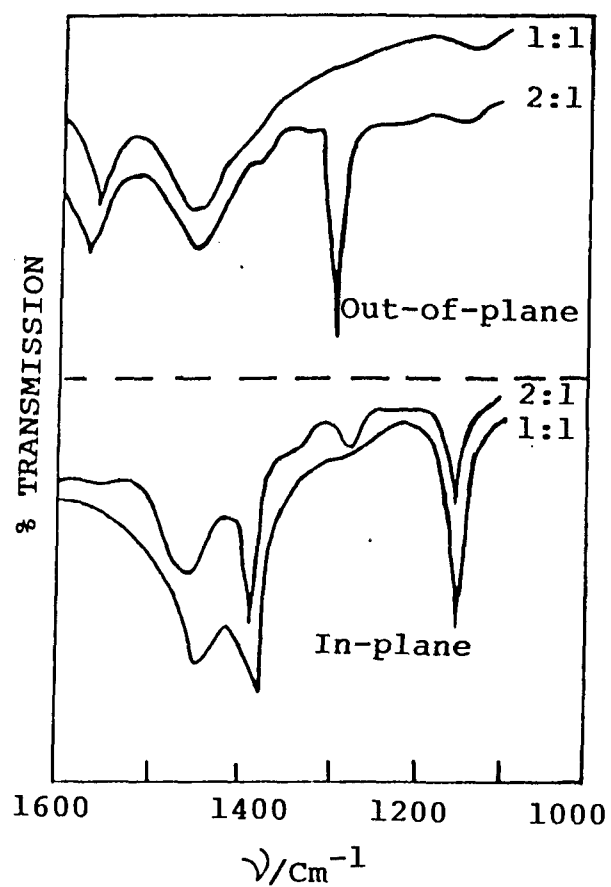


Fig. 5 Infrared spectra in the 1100-1600 cm^{-1} range for the 1:1 & 2:1 crystalline complexes of hexamethylbenzene and tetracyanethylene.

compounds are capable of forming both the electron transfer complexes and those comprising proton donation to the donor. 2,4-Dinitrotoluene (DNT) is a non acidic acceptor and, therefore, it is expected to display the general spectral shifts of π - π^* complexes⁷². Since the stability of these complexes arises from a shift of the electron density from the donor to the electron deficient acceptor molecule, the infra-red region should record the effect of the change of electron density in the components upon the vibration of atoms within the individual molecules. Study of vibrational spectra may also reveal which parts of the molecules play an active role in complex formation.

1.5 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Just like IR, NMR spectrometry of CT complexes gives a summation of the spectra of the individual reactants. On complex formation electron density is transferred from the donor to the acceptor; the electron density around the acceptor protons is increased and the electron density around the donor protons is decreased, giving rise to an upfield shift of the protons of the acceptor and a down field shift of the protons of the donor.

1.6 SPECTROPHOTOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANT AND MOLAR ABSORPTIVITY

The formation constant is defined for the reaction



by the expression:

$$K = \frac{[AD]}{[A][D]} \quad \dots (18)$$

Here, for example, $[D]$ is the concentration (in moles per litre) of the donor that exists in the solution at equilibrium. If we take solutions with a fixed total concentration $[A]_0$ of A but with increasing concentrations of D, equation (18) implies that the concentration $[AD]$ of the complex AD increases as shown in Figure 6. (The absorption observed may be that of the CT band or it could be absorption for a locally excited band of D or A, shifted in the complex). Since the absorbance A due to AD in a region in which the complex absorbs is given by Beer's law.

$$A = \log \frac{I_0}{I} = \epsilon [AD] l$$

Here ϵ is the molar absorptivity of AD and l is the length in centimeters of the absorbing path. The value of A must increase as $[D]$ increases, as is seen from Figure 6, depending on how large K is, $[AD]$ at maximum possible donor concentration (region III of Figure 6, $K > 1.0$) or be

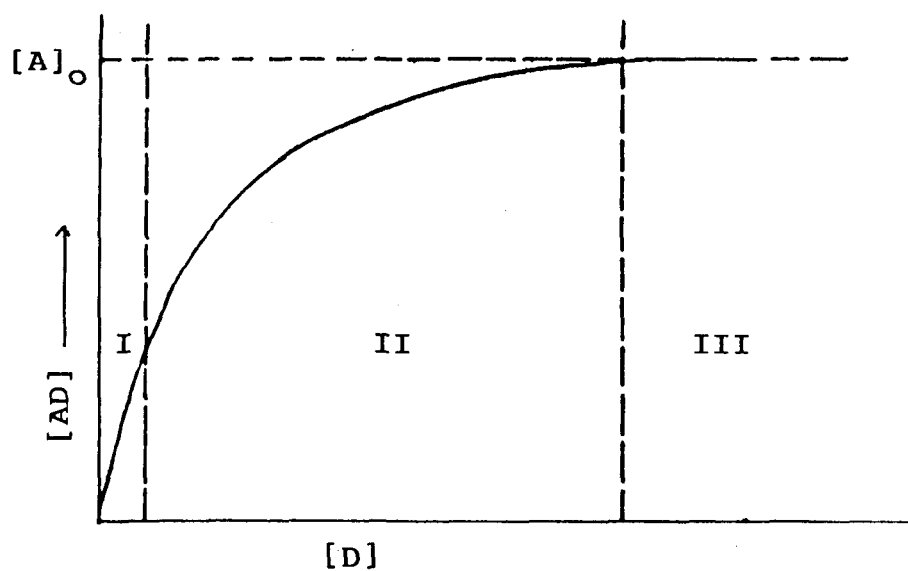


Fig. 6 The concentration of complex as a function of donor concentration for a fixed total acceptor concentration $[A]_0$. Region I: $[AD]$ is approximately a linear function of $[D]$. Region III: Saturation has been reached, and $[AD]$ is constant and equal to $[A]_0$.

limited to region II ($K \approx 0.1$) or even to region I ($K < 0.01$). (In the latter two cases the $[D]$ scale in Figure 6 would, of course, be modified).

As a specific example, the visible spectrum of the complex between pyridine-N-oxide and I_2 is shown in Figure 7. This figure illustrates the increasing absorbance near 450 nm of the complexed I_2 and the decreasing absorbance near 520 nm due to the familiar locally excited band of uncomplexed I_2 as the concentration of donor is increased, with an isobestic point at 490 nm. The existence of this point confirms the assumption that only two species in the solution (complexed I_2 and uncomplexed I_2) absorb in this region of the spectrum.

Figure 7 also illustrates the problem of overlapping absorption of two species which often occurs. In principle a correction is made for the absorbance due to the uncomplexed I_2 in order that the absorbance due to the complex alone may be obtained (illustrated by curve 6 in figure 7). In practice the details of this correction may be somewhat troublesome; for example we determine ϵ_A for the acceptor alone in a solvent and compute the correction A_A to be subtracted from the total absorbance A_T to obtain A , the absorbance of the complex AD. In doing so we usually assume that the absorption for uncomplexed A does not change when the solvent is changed by adding D. This assumption is

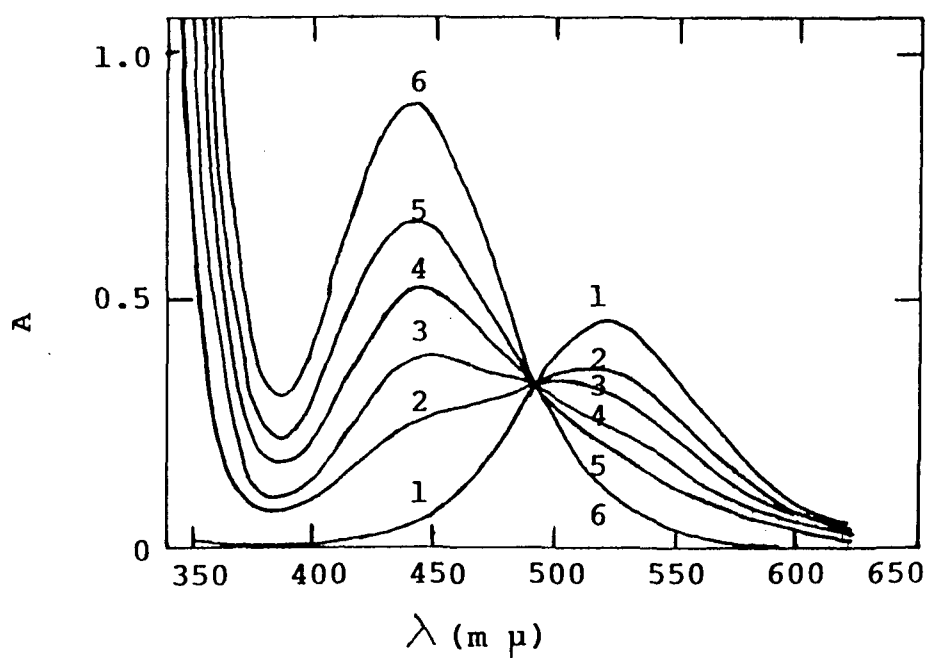


Fig. 7 The visible absorption spectrum of pyridine-N-oxide-iodine in carbon tetrachloride (23°C, 5-cm cell). Curve 1 is for iodine ($9.550 \times 10^{-5} \text{M}$). The concentration of pyridine-N-oxide are $4.210 \times 10^{-3} \text{M}$ for curve 2, $8.421 \times 10^{-3} \text{M}$ for curve 3, $16.84 \times 10^{-3} \text{M}$ curve 4 and $33.68 \times 10^{-3} \text{M}$ for curve 5; curve 6 is a calculated curve for the absorption that is due solely to the complexed iodine molecule. (From T.Kubota, J. Am. Chem. Soc., 87, 458 (1965)).

at best questionable in the case of weak complexes, for which $[D]$ has to be made rather large.

From the corrected absorbance A at a given frequency ν for a series of concentration $[D]$, the values of K and ϵ_ν can be obtained using the method of Benesi and Hildebrand⁸. The Benesi-Hildebrand analysis starts from the assumption that only one equilibrium exists in the solution and that the constant is defined as in (18). Then, using a zero superscript to denote the total concentration ($[D]_0 = [D] + [AD]$, etc.), we have,

$$\frac{1}{K} = \frac{[D]_0 - [AD]}{[AD]} \frac{[A]_0 - [AD]}{[AD]} - \frac{[D]_0[A]_0 - [D]_0}{[AD]} - [A]_0 + [AD] \quad \dots (19)$$

under the usual conditions (K small, A relatively insoluble) $[D]_0$ is very much greater than $[A]_0$, in order to form enough complex: $[D]_0 \gg [A]_0 > [AD]$. From Beer's Law $[AD] = A/\epsilon_\nu l$; hence to a good approximation.

$$\frac{1}{K} = \frac{1[D]_0 [A]_0 \epsilon_\nu}{A} - [D]_0 \quad \dots (20)$$

Dividing by $[D]_0 \epsilon_\nu$ and rearranging, we obtain the Benesi-Hildebrand equation:

$$\frac{1[A]_0}{A} = \frac{1}{K \epsilon_\nu} \frac{1}{[D]_0} + \frac{1}{\epsilon_\nu} \quad \dots (21)$$

Here in a given experiment we know l , $[A]_0$ and $[D]_0$; A is measured for a series of solutions with varying $[D]_0$, and the

results are plotted as shown in Figure 8. From the slope and intercept the values of K and ϵ_v can be obtained.

The above equation is not valid for sparingly soluble compounds because their concentrations cannot be accurately determined, therefore, the Pushkin-Varshney-Kamoonpuri⁷³ equation was proposed to solve this problem. This equation takes the form

$$\frac{1}{A} = \frac{1}{K \epsilon_v} \cdot \frac{1}{[A]_0} \cdot \frac{1}{[D]_0} + \frac{1}{[A]_0 \epsilon_v} \quad \dots (22)$$

If a plot is made of $1/A$ versus $1/[D]_0$ a straight line is obtained and K is evaluated by dividing the intercept by the slope. Therefore, $[A]_0$ mutually cancels out and is not required for evaluation of K . $[A]_0$ should be kept constant in all solutions.

1.6.1 DETERMINATION OF OTHER THERMODYNAMIC PROPERTIES

We can obtain ΔH° from measurement of K at more than one temperature using the van't Hoff equation⁷⁴

$$\ln K = - \frac{H^\circ}{R} \cdot \frac{1}{T} + \frac{S^\circ}{R} \quad \dots (23)$$

Assuming that ΔH° is constant over the temperature range involved, a plot of $\ln K$ against $1/T$ should then be a straight line whose slope gives ΔH° and whose intercept is

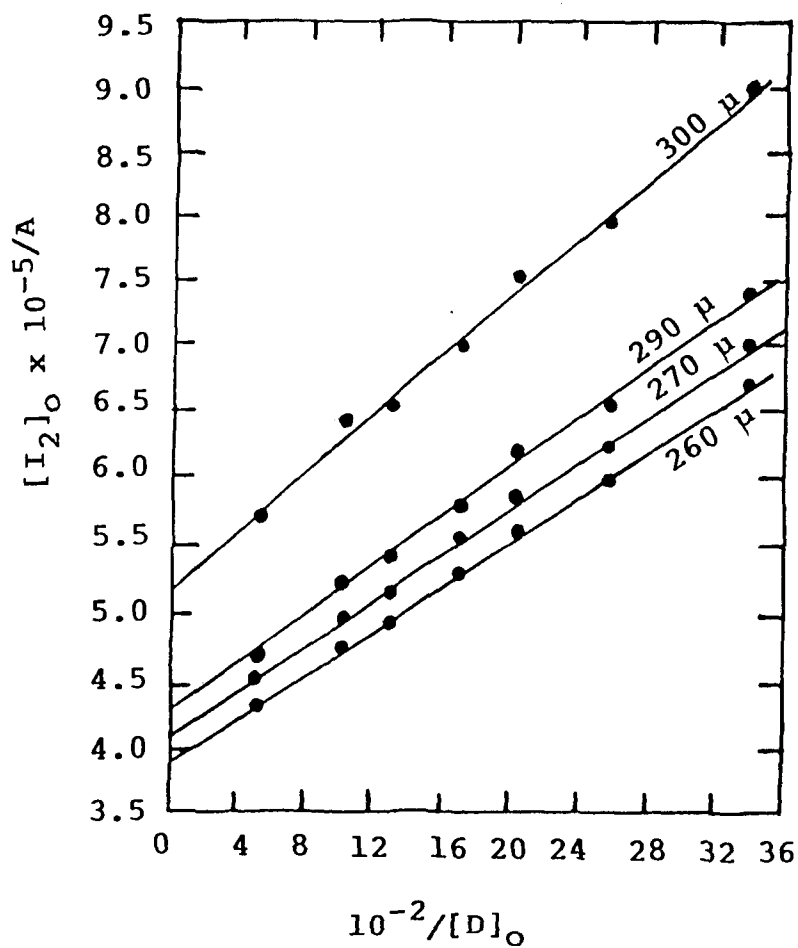


Fig. 8 Illustration of the use of the Benesi-Hildebrand equation to obtain K and ϵ_v at four wavelenths for the Triethylamine. I_2 Complex, the intercept of each line is $1/\epsilon_v$; the slope is $(1/K\epsilon_v)$. [From S. Nagakura, J. Am. Chem. Soc., 80, 520 (1958)].

$\Delta S^\circ/R$. In this way the enthalpy change ΔH° and the standard entropy change ΔS° for complex formation can be obtained.

1.6.2 DETERMINATION OF EQUILIBRIUM CONSTANT BY IR SPECTROMETRY

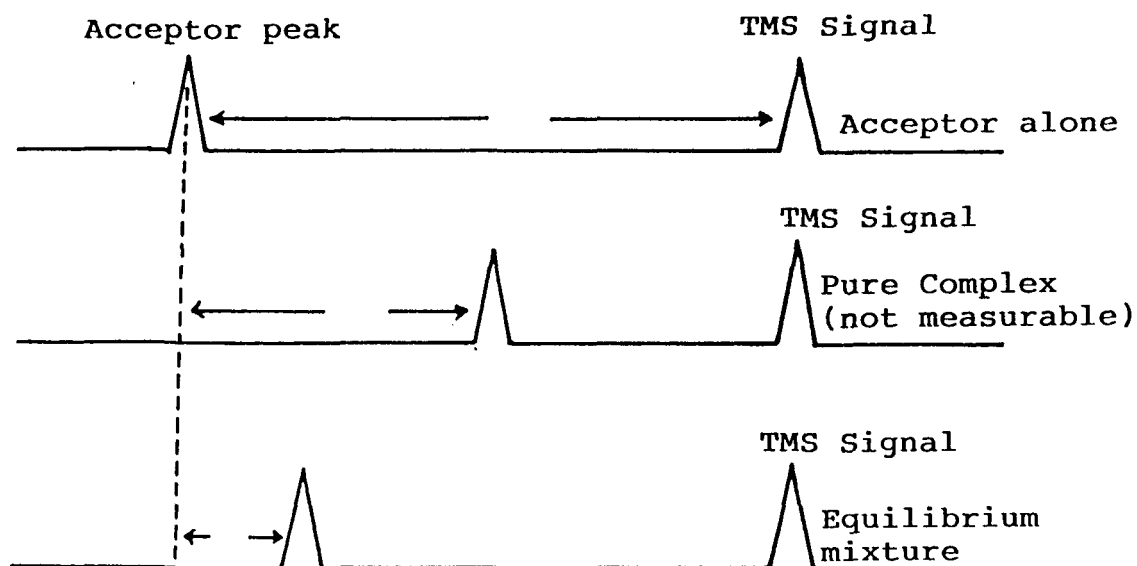
Though charge-transfer complexes have mainly been studied by UV-visible spectroscopy chiefly due to the possible isolation of the charge-transfer band, IR spectrometry can give an idea about the geometry of the complex. In most complexes and specially in the weaker ones the IR spectra is merely a summation of the individual spectra. However, shifting of peaks may take place to lower or higher frequencies. The regions where there is a greater shift in electron density are the ones that give rise to more prominent peaks; enhanced intensity and greater magnitude in the frequency shifts.

IR spectrometry can also be used to determine the association constants using the usual Benesi-Hildebrand equation (21). For this it is necessary that a peak is chosen which is not overlapped by other peaks and has maximum intensity. The transmittance is measured and converted to absorbance directly. IR spectrometry is a useful tool to distinguish between charge-transfer and hydrogen bonding. For example, if aniline is involved in

hydrogen bonding the N-H vibration in the complex will move to lower frequencies while in the case of charge-transfer the reverse will be true. IR is also diagnostic of those CT complexes where there is almost complete transfer of an electron from the donor to the acceptor and highly conducting organic metals or semiconductors result. In this case there is usually no peak in the entire IR region.

1.6.3 DETERMINATION OF EQUILIBRIUM CONSTANT BY NMR SPECTROMETRY

There is a difference in evaluating association constants by NMR spectrometry than in electronic or IR spectroscopy. In this case the method of Hanna and Ashbaugh⁷⁵ is used. The method is as follows: A small amount of the acceptor with a large amount of the donor is dissolved in an inert solvent like CCl_4 . The acceptor concentration is kept constant while the donor concentration is varied. The various shifts are shown schematically below:



The association constant is obtained according to equation:

$$\frac{1}{\Delta} = \frac{1}{K} \cdot \frac{1}{\Delta_o} \cdot \frac{1}{[D]_o} + \frac{1}{\Delta_o} \dots (24)$$

where $\frac{1}{\Delta}$ is plotted against $\frac{1}{[D]_o}$ and K and Δ_o are evaluated from the slope and the intercept.

In addition to this the Qureshi-Varshney-Kamoonpuri equation⁷⁶ proposed recently outlines a method for the first time in NMR to ascertain whether the activity coefficients are unity or show deviations. The Qureshi-Varshney-Kamoonpuri equation takes the form

$$\frac{[D]_o}{\Delta} = \frac{1}{K} \cdot \frac{1}{\Delta_o} + \frac{[D]_o}{\Delta_o} \dots (25)$$

A plot of $[D]_o/\Delta$ vs $[D]_o$ should yield a straight line with the slope giving Δ_o and K is then obtained from the intercept.

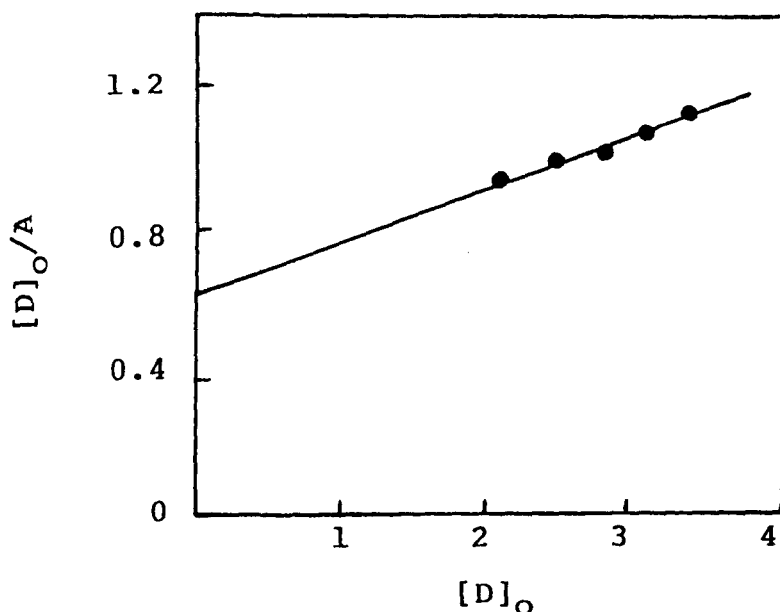


Fig. 9 A typical Qureshi-Varshney-Kamoonpuri plot

1.7 SOME RECENT DEVELOPMENTS IN CHARGE-TRANSFER COMPLEXES

Equilibrium measurements have been used for the evaluation of ionization potentials⁷⁷. Though such studies leave much to be desired by way of accuracy, nevertheless, they are important due to their inherent simplicity. The space interactions and reactivity have been related by studying the photoelectron and charge-transfer spectra of benzobicycloalkenes⁷⁸. Studies in micellar media are gaining a unique importance in chemistry and, therefore, it is interesting to note, a recent report showing the effect of micelles on the state and dynamics of some excited charge-transfer complexes⁷⁹. The formation constants of selected charge-transfer complexes have been measured using a

computer controlled precision polarograph⁸⁰. It has been shown that flavin mononucleotide forms charge-transfer complexes with phenols. This has been established through the use of resonance Raman spectroscopy⁸¹. A single crystal of the charge-transfer complex between hexaethylbenzene and tetracyanoethylene was investigated for conformational effects and for charge-transfer transitions⁸². Conducting organic charge-transfer complexes are of current importance due to their possible use as organic conductors, semiconductors and therefore, it is interesting to note that the charge-transfer salts synthesized by the reaction of tetrathiafulvalenes and tetrahalo-p-benzoquinones produced highly conducting organic materials⁸³. It was shown that the complexes of phenylfurans and tetracyanoethylene were $\pi-\pi^*$ complexes⁸⁴. In an excellent study it has been shown that some charge-transfer complexes of tetracyanoquinodimethane can be used to prepare electrochemical electrodes which can be used over a potential region where they serve as inert electrodes⁸⁵. Most of the organic conductors to date have been based on tetracyanoquinodimethane. Therefore it is very encouraging to note that the charge-transfer compounds composed of tetrathiafulvalene and chloranil are perhaps the first highly conducting organic materials that do not contain tetracyanoquinodimethane⁸⁶. IR spectroscopy has been used to study the degree of charge-transfer in organic conductors⁸⁷,

$n-\pi^*$ charge-transfer complexes are now systematically being studied due to the paucity of such studies on this important family of complexes. For example, the interaction of aliphatic amines and benzonitrile has been reported⁸⁸. The solvent effects on the charge-transfer spectra of some aminoanthraquinone dyes have been reported in nine different solvents⁸⁹. Surface enhanced Raman scattering shows that there is a charge-transfer from tetrathiafulvalene to silver and gold⁹⁰. The formation of a charge-transfer complex between quinoline and boron tetrafluoride leads to significant changes in the ordering of electronic levels effecting fluorescence, phosphorescence and inter-system crossing⁹¹. The mechanism of electron transfer from dihydronicotinamide adenine dinucleotide (NADH) to p-benzoquinone derivatives has been shown to proceed via a charge-transfer complex⁹². Picosecond laser photolysis has been used to establish the charge-transfer process that occurs in the dibenzocarbazolepyridine hydrogen bonded complexes as a function of structure⁹³. The 1:1 and 2:1 complexes of hexamethylbenzene with tetracyanoethylene have been studied by resonance Raman spectroscopy⁹⁴. The colour of (nitrophenyl) anilines has been explained from an x-ray crystallographic study that indicates that the molecules are placed in a "head-to-tail" arrangement resulting in an unusual charge-transfer between two molecules of the same

compound⁹⁵. Some large electron acceptors based on various substituted quinodimethanes, have been designated as acceptors for molecular metals⁹⁶. The study of vapour-phase charge-transfer complexes is rather difficult owing to the sophistication and cost of instrumentation. It is due to this reason that not much progress has been made in this important direction. It is, therefore, encouraging to note that electron energy loss spectroscopy has been used for the investigation of vapour-phase charge-transfer complexes of halogens with n-donors⁹⁷. Graphite coated with viologen polymers behaves as an electrode via a charge-transfer process⁹⁸. Charge-transfer complexes have been used for the synthesis of organic ferromagnetic materials⁹⁹. The trimethylamine-sulphur dioxide system is the only system for reaction thermodynamics are known both in solution and gas phase. The microwave spectrum of this system has been studied in order to elucidate the structure of the complex¹⁰⁰. The reaction of azoalkanes with series of donors which are both sacrificial (π^*, σ^*) and inerevalent gives rise to charge-transfer complexation¹⁰¹. The fluorescence spectrum of benzenilide exhibits the anomaly that its λ_{max} occurs at longer wavelengths than that of its phosphorescence emission. It has recently¹⁰² been shown that this anomaly may be due to an intramolecular charge-transfer transition. A new approximate procedure for the

determination of enthalpy of formation and formation constants of weakly bonded charge-transfer complexes has been reported and has been applied to complexes of molecular iodine and chlorinated benzenes¹⁰³. The effect of solvent on dipole moment and charge-transfer in electron systems has been studied in N,N-dimethyl-p-nitrosoaniline¹⁰⁴. ¹H NMR spectrometry¹⁰⁵ has been used to evaluate association constants for the electron-donor-acceptor complexes for the complexes of indoles and substituted indoles with 1-(2,4,6-trinitrophenyl) propan-7-one. It has been suggested that both internal and external references may be eliminated in NMR determinations of fast equilibria with special reference to charge-transfer complexes¹⁰⁶. This study also questions the use of tetramethylsilane (TMS) as an internal reference due to the possibility that TMS may not be as inert as assumed. A new and simple development for the measurement of charge-transfer through fibre optic photometry has been proposed¹⁰⁷. The preparation and solid-state characterization and X-ray crystal structure of the 1:1 charge-transfer complex of tetrathiafulvalene and m-dinitrobenzene is an important landmark in the study of charge-transfer complexes of polynitroaromatics¹⁰⁸. When liquid and film polymeric compositions like polyurethanes, polyethylene glycol-115 and styrene-methacrylate-acrylonitrile copolymer

are doped with anion-radical salts like NaTCNQ in the presence of crown ethers, their conductivities increase due to charge-transfer complexation¹⁰⁹. An spectrophotometric assay of certain cardiovascular drugs through their charge-transfer complexes with p-chloranilic acid, dichlorophenylindophenol and 2,3-dichloro-5,6-dicyano-p-benzoquinone has been described¹¹⁰. In an interesting study it has been shown that the tropylium cation ($C_7H_7^+$) forms donor-acceptor complexes with various benzene, naphthalene and anthracene donors signified by bright coloured solutions and linear relationships with arene ionization potentials¹¹¹. Spectroscopic studies on charge-transfer complexes of trivalent phosphorous compounds like triphenylphosphine with maleic anhydride have been carried out¹¹². A conductometric titration technique has been used for determining the stoichiometry of charge-transfer complexes which ionize in polar media¹¹³. Mainly complexes of iodine have been studied. Charge-transfer complexes formed by a discogenic electron donor (2,3,6,7,10,11- hexa-n-pentyloxytriphenylene) and a non-discogenic electron acceptor (2,4,7-trinitrofluoren-9-one) in non-polar solvents are studied by pico-second time-resolved absorption spectroscopy based on Kerr ellipsometry¹¹⁴. Charge-transfer complexes formed between various para-substituted benzoyl chlorides and triethylamine in acetonitrile have been studied spectrophotometrically¹¹⁵.

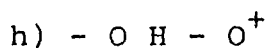
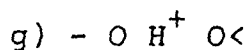
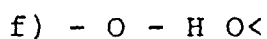
The N-nitrosopyridinium cation (PyNO^+) forms a series of intermolecular EDA complexes with aromatic hydrocarbons which show distinctive charge-transfer absorption bands in the visible region¹¹⁶.

1.8 HYDROGEN BONDING

Many investigations have been carried out on the inter- and intra-molecular interactions among proton donors like $-\text{OH}$, $-\text{NH}_2$, etc., and proton acceptors such as amines and oxo-compounds. It has been well verified that hydrogen bonding in molecular complexes (frequently written, for example, as $-\text{O}-\text{H}\cdots\text{O}<$) is formed between proton donors and acceptors. Since atoms participating in the hydrogen bond formation are usually electronegative atoms such as F (halogen), O, and N, and moreover, since a hydrogen atom has a small size, which makes it possible for it to occupy a position closer to a proton acceptor than can other elements, the force to bring about the hydrogen bonding has been mainly attributed to the electrostatic force. For instance, energy calculations according to the electrostatic model were made by Coggeshall¹¹⁷ for some hydrogen bonding systems. The results of the calculations seemed to be in satisfactory agreement with experimental ones. However, it is supposed that there is no reason to reject the contribution from the covalent bonding interaction nature to the hydrogen bond formation. The covalent bonding nature has

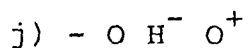
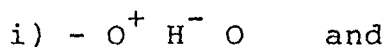
been a central problem of the experimental and theoretical studies of hydrogen bonding since about 1950. Among many workers this problem was especially discussed by Mulliken¹¹⁸⁻¹²⁰ Nagakura et al^{121,122}, Coulson and Danielsson¹²³⁻¹²⁵, Tsubomura¹²⁶, Pimentel¹²⁷, and Murrell et al¹²⁸.

In valence bond language the main resonance forms of a hydrogen bonding system would be written as below, for a typical example of an O - H ... O system.



Here, structures f and g correspond to the no-bond structure in terms of charge-transfer theory. Structure f means a pure covalent pairing between an oxygen orbital and a hydrogen orbital. Structure g is a purely ionic structure of the OH bond and could mainly cause an electrostatic interaction with a proton acceptor. Structure h is a charge-transfer structure where the long covalent bond is formed between the H atom and the oxygen atom of proton acceptor. This structure h should play an important role in the covalent nature of hydrogen bonding.

Of course there are other resonance forms such as



The contributions from these resonance structures, however, seem to be smaller than those from the structures f, g and h, since chemical and physicochemical evidence shows the O-H bond to have polarization $O^{\delta-} - H^{\delta+}$.

In molecular orbital language the contribution from the charge-transfer resonance structure h would be explained as follows: When one takes into account only the O-H σ bond and the lone pair orbital of proton acceptors, the mutual relation of energy levels among the σ bonding, σ^* antibonding, and the lone pair orbital may be illustrated as in Fig. 10.

Resonance structure h should be due to an electron transfer from the ψ_{01} orbital to the σ^* antibonding orbital. Because of the antibonding nature of the σ^* orbital the aforementioned electron-transfer should inevitably weaken the OH bond, as can be seen in the resonance structure h, so that the O-H σ bond distance becomes longer than in the normal one, and a new and long H-O δ^+ bond is formed.

These results will cause a double minimum potential pertinent to the hydrogen bonding system. It should be now noted that the characteristic of the antibonding σ^* orbital of an O-H group and that of halogen molecules like iodine are somewhat similar to each other, as indicated in Fig. 11. Thus the n- σ type halogen complex or the n- σ type hydrogen bonding complex will be formed so as to satisfy the

maximum overlap between the plus lobe (k) or (l) shown in Fig. 11 and the nobonding electron donor orbital. Therefore, we can understand that the geometrical arrangements of the n- σ type halogen complex and hydrogen bonding complex are quite similar to each other.

The theoretical considerations show that the contribution of the charge-transfer type of force cannot be neglected as a source of hydrogen bonding energy. Many experimental facts supporting this viewpoint have been reported by many workers. From the concept of charge-transfer theory the charge-transfer energy pertinent to hydrogen bonding may be mainly attributed to consideration of the quantum mechanical resonance between the following two resonance forms: $[X-H...Y] \longleftrightarrow [X^-... H^+Y]$. The nature of the electronic interaction in the hydrogen bonding and the n- σ type charge-transfer complexes is quite similar. Therefore, it seems to be quite reasonable to expect the appearance of a charge-transfer spectrum due to the hydrogen bonded complex in a suitable wavelength region, depending on the nature of the hydrogen bonding system. The effort to detect the charge-transfer spectra pertinent to hydrogen bonding was carried on by many workers. But clear detection of this kind of charge-transfer spectra was found to be quite difficult because, the charge-transfer spectra possibly occur in a region of the far-UV (less than 220 m μ)

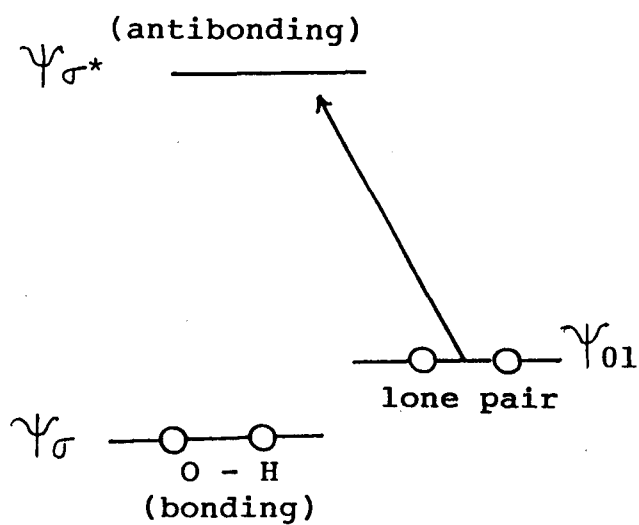


Fig. 10 Simple MO description of hydrogen bonding system, $\text{O}-\text{H}\cdots\text{O}<$.

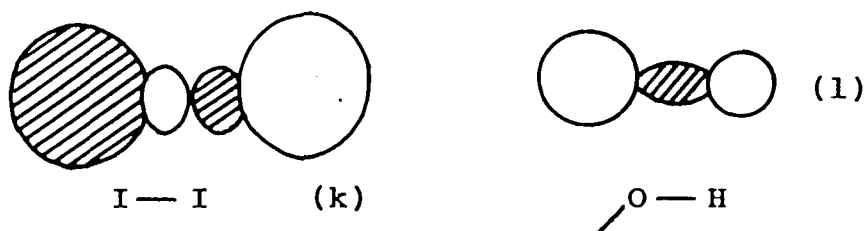
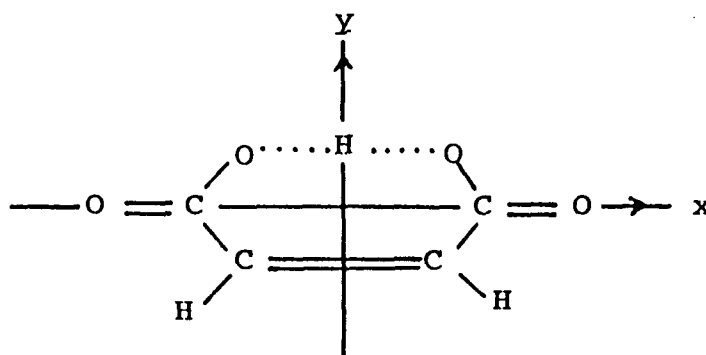


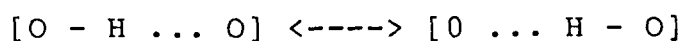
Fig. 11 Schematic representation of σ^* antibonding orbital of I_2 and $\text{O}-\text{H}$ bond. Each size means the negative part of orbitals.

where electronic spectra originating, e.g., from a $n-\sigma^*$ type transition or a Rydberg transition appear. Moreover, quantitative measurement of absorption spectra is not so easy in the far-UV region.

Among the studies of hydrogen bonding reported up to now, however, there is an example of the charge-transfer spectrum caused by the relatively strong intra-molecular hydrogen bond of mononegative ion of maleic acid (MNMA)¹²².



Because of the symmetrical structure of the hydrogen maleate anion the hydrogen atom participating in the hydrogen bonding is placed at the mid-point between two oxygens. Actually this structure has been confirmed by X-ray analysis of crystalline MNMA^{129,130}. Atomic orbitals participating in the system of the hydrogen bond $O \cdots H \cdots O$ are in the molecular plane of MNMA and are perpendicular to the π type atomic orbitals (π electron system). Therefore, the electronic interaction in the hydrogen bond will be approximately represented by the resonance between two structures with equal energies:



Mutual interaction between Ψ_A and Ψ_B produces two new wave functions, Ψ_N and Ψ_E , the former being for ground state with eigen-value W_N and the latter for the excited state having the energy W_E ¹²².

$$\Psi_N = \frac{1}{\sqrt{2(1 + S_{AB})}} (\Psi_A + \Psi_B) \quad \dots (26)$$

$$\Psi_E = \frac{1}{\sqrt{2(1 - S_{AB})}} (\Psi_A - \Psi_B) \quad \dots (27)$$

W_N and W_E are now given by usual method:

$$W_N = \frac{H_{AB}}{1 + S_{BA}} \quad \text{and} \quad W_E = \frac{-H_{AB}}{1 - S_{AB}} \quad \dots (28)$$

Here, the energy of Ψ_A and Ψ_B is taken as a standard (energy zero). Thus the energy of the charge-transfer spectrum becomes

$$W = W_E - W_N = \frac{-2H_{AB}}{1 - S_{AB}^2} \quad \dots (29)$$

and the oscillating strength is calculated, using the well-known equation

$$f = 1.085 \times 10^{-5} \times \tilde{\nu}_Q^2 \quad \dots (30)$$

where ν is the transition energy (cm^{-1} unit) and Q is the transition dipole length (\AA unit). Remembering the ψ_A or ψ_B in equations (26) and (27) the calculation¹²³ of S_{AB} results in $2(S_{OH})^2$, where S_{OH} means the overlap intergral between appropriate atomic wave functions for the oxygen and hydrogen atoms. Thus Nagakura¹²² evaluated the oscillator strength f , using the calculated value (0.279) of S_{OH} and the observed charge-transfer maximum 211 m μ , $f = 0.78$ being obtained. This result may suggest that the charge-transfer spectrum brought about by hydrogen bonding should have quite strong intensity. Experimentally, the UV spectra of the hydrogen maleate anion were examined by Nagakura at various pH values in aqueous solution and also by the measurement of polarized spectra of the single crystal of potassium hydrogen maleate, the data being depicted in figures 12 and 13¹²².

Curve 1 in figure 12 is for maleic acid (MH_2), curve 2 for the monoanion (MH^-), and curve 3 could be due to the dianion (M^{2-}) plus a small quantity of MH^- . It is now certain from figures 12 and 13 that the absorption band due to MH^- is in high intensity and that the 211-mu band of MH^- shows stronger absorption with the light polarized along the c axis than when along the b axis. The combination of these spectral data with those of X-ray analyses of the MH^- crystal led to the conclusion that the 211 m μ band is polarized along the O - H ... O bonds.

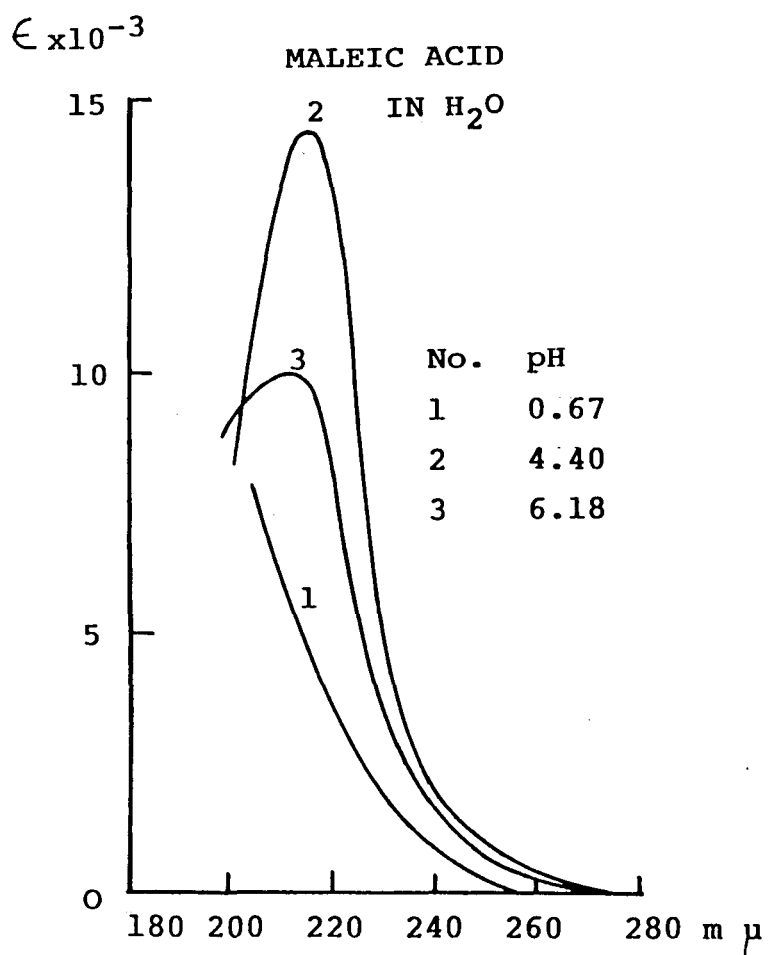


Fig. 12 Absorption spectra of aqueous solutions of maleic acid at pH=0.67 (curve 1), 4.40 (curve 2), and 6.18 (curve 3).

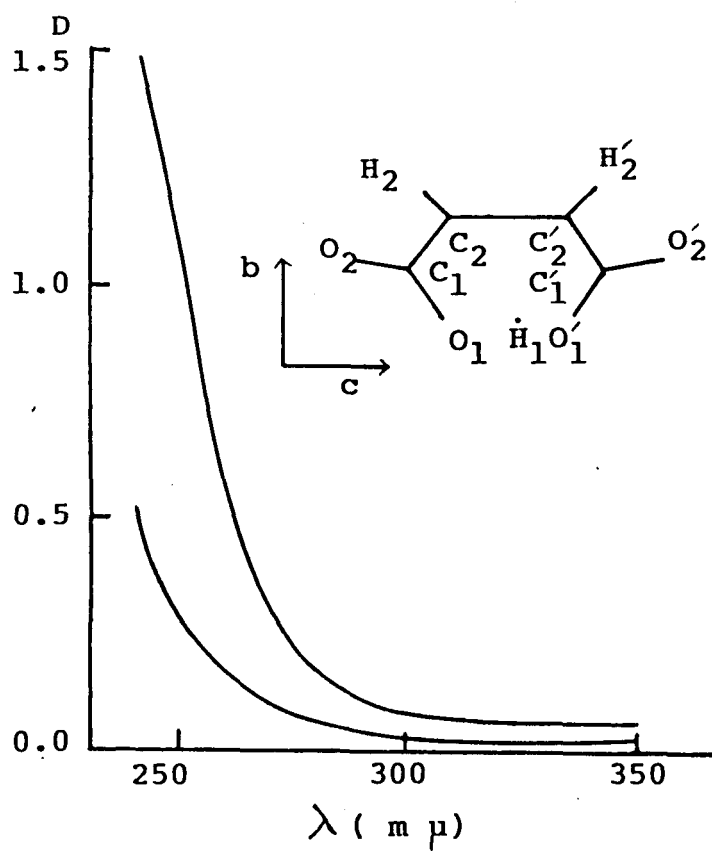


Fig. 13 Polarized ultraviolet absorption measured with a potassium hydrogen maleate single crystal.

Moreover, it should be noted that the $\pi-\pi^*$ absorption band of the species M^{2-} should appear at a wavelength longer than that of the species MH^- . The result of the theoretical P.P.P. type calculation supported this conclusion¹²². Since it is clear from figure 12 that the 211-mu band in question shifts to a shorter wavelength in the medium where the molecule exists predominantly as the M^{2-} species, the assignment of the 211 mμ band to the $\pi-\pi^*$ transition may not be reasonable. Nagakura suggested that the band should be attributed to the charge-transfer band pertinent to the hydrogen bonding system in the MH^- molecule.

Charge-Transfer forces play an important role in the hydrogen bonding interaction. Some experimental results which support this conclusion will be described in this section. One examines here the proton accepting power of some typical compounds. First, are triethylamine, diethyl-ether, and nitromethane¹³¹. The dipole moment of these compounds increases in this order, as is seen in Table 3 where many data are collected for comparison. If the nature of the hydrogen bond is essentially electrostatic, then one supposes that the hydrogen bonding power is of the order of $CH_3NO_2 > O(C_2H_5)_2 > N(C_2H_5)_3$. Actually, however, this is not the case, as Table 3 shows. So the electrostatic interaction seems not to be the main source for the present hydrogen bonding interaction. On the other hand, the ionization

potential I_p is in the order: $N(C_2H_5)_3 < O(C_2H_5)_2 < CH_3NO_2$. This order is just the reverse of the observed one of the hydrogen bonding ability i.e. $N(C_2H_5)_3 > O(C_2H_5)_2 > CH_3NO_2$ but is in agreement with that predicted by Eq. (31),

$$\Delta E = - \frac{2 \beta_Y^2 - H_X}{I_Y - A_{X-H}} \quad \dots (31)$$

where ΔE is delocalization energy, I_Y and A_{X-H} are the ionization potential of the occupied orbital of the proton acceptor and electron affinity of the vacant σ^* orbital of the X-H bond respectively, β_{Y-HX} is the resonance integral between the ψ_D and ψ_{σ^*} orbitals, which describes the stabilization energy of the hydrogen bond due to the charge-transfer mechanism. Therefore, it seems that the charge-transfer force will contribute more predominantly to the hydrogen bonding systems mentioned above. The same conclusion as has been described above was also derived from the comparison of the proton accepting power among triethylamine, ethyl acetate, and acetonitrile¹³². The values of the equilibrium constant K of the hydrogen bond formation with β -naphthol in the ground state are in the order (see Table 3) of $(C_2H_5)_3N > CH_3COOC_2H_5 > CH_3CN$. Since the order of I_p is $(C_2H_5)_3N < CH_3COOC_2H_5 < CH_3CN$, again decreasing the value of equilibrium constant K . Furthermore, the red shift of the 1L_b band of β -naphthol caused by the hydrogen bonding interaction is largest in the case of $(C_2H_5)_3N$ and smallest for CH_3CN .

TABLE 3

HYDROGEN BONDING AND IODINE COMPLEXING ABILITIES AND OTHER NATURES OF SOME ELECTRON DONORS

Proton donor	Proton acceptor	Equilibrium constant K(litre/mole)	Shift of absorption spectra of proton donor (cm^{-1})	Acceptor		
				$I_p(\text{ev})$	pK_a	Dipole moment
β -naphthol	$\text{N}(\text{C}_2\text{H}_5)_3$	103 (25°C)	590 ($^1\text{L}_b$ band)	7.5	10.72	0.82
(n-heptane)	$\text{O}(\text{C}_2\text{H}_5)_2$	14.5 (25°C)	410 ($^1\text{L}_b$ band)	9.53	-3 to -3.61	1.13
	$\text{CH}_3\cdot\text{NO}_2$	2.6 (25°C)	190 ($^1\text{L}_b$ band)	10.33 11.32	-11.38	3.50
β -naphthol	$\text{N}(\text{C}_2\text{H}_5)_3$	180 ($\sim 15^\circ\text{C}$)	590 ($^1\text{L}_b$ band)	7.5	10.72	0.82
(cyclohexane)	$\text{CH}_3\text{COOC}_2\text{H}_5$	14 ($\sim 15^\circ\text{C}$)	310 ($^1\text{L}_b$ band)	10.09	-6.2	1.83
	CH_3CN	9 ($\sim 15^\circ\text{C}$)	200 ($^1\text{L}_b$ band)	12.39		3.92 3.47
Electron donor	Electron acceptor	Equilibrium constant K(litre/mole)	Heat of formation (kcal/mole)	pK_a of electron donor		
$\text{N}(\text{C}_2\text{H}_5)_3$	I_2 (n-heptane)	6460 (20°C)	12			10.72
$\text{C}_6\text{H}_5\cdot\text{N}(\text{CH}_3)_2$	I_2 (n-heptane)	41.0 (11°C)	8.2			5.21
$\text{C}_6\text{H}_5\cdot\text{C}\equiv\text{N}$	I_2 (CCl_4)	0.81 (20°C)	-			-

1.9 SOME RECENT AND IMPORTANT DEVELOPMENTS IN HYDROGEN BONDING ARE AS FOLLOWS

A study has been carried out by IR spectrometry to study hydrogen bonding in simple and complex ammonium halides¹³³. The ^{15}N chemical shifts of N-methylpyrazole, 3-methyl, and 3,5-dimethylpyrazole and indazole have been measured as a function of solvent and acidity of the medium¹³⁴. It was observed that hydrogen bonding and protonation resulted in upfield shifts of both the pyridine and pyrrole type resonances. Evidence, by X-ray diffraction shows the presence of a C-H...O hydrogen bond in the organic metal formed by the interaction of tetrathiafulvalene and chloranil¹³⁵. It has been shown that hydrogen bonding in $(\text{Et}_3\text{NH})_2\text{SnCl}_6$ is stronger than in the corresponding ammonium compound³⁶. Empirical lattice energy calculations have been reported to determine the potential parameters for phosphate hydrogen bonds¹³⁷. Picosecond dynamics reveal that the $\pi-\pi^*$ ketones remain hydrogen bonded in the excited state¹³⁸. Solvent effects on amine-n-butyl alcohol hydrogen bonded complexes have been studied by calorimetry¹³⁹. A similar study reports the solvent effect on the hydrogen bonded complex between adenine and uracil by calorimetry, and theoretical calculations¹⁴⁰. The intramolecular hydrogen bond of 6-hydroxybenzanthrone has been investigated by fluorescence, phosphorescence, and luminescence excitation spectrometry¹⁴¹. An interesting study of the solvent effect

on the spectra of benoxaprofen revealed that while the absorption maxima did not respond to solvent change the fluorescence maxima was very much solvent sensitive and shifts to longer wavelengths as the hydrogen bonding ability and the polarity of the solvent increases¹⁴². The hydrogen bonding basicity of amidines has been measured by frequency shift $\Delta\nu(\text{OH})$ of methanol hydrogen bonded to amidines, and, the electronic and steric effects investigated¹⁴³. Theoretical studies have been carried out of vibrational frequency shifts on hydrogen bonding¹⁴⁴. Amphiphilic self assembly has shown to be essentially due to hydrogen bonding¹⁴⁵. A scale of solute hydrogen-bond acidity employing equilibrium constant has been devised¹⁴⁶. Bilirubins and Biliverdins have been distinguished by their pronounced tendency to form inter- and/or intra-molecular hydrogen bonds¹⁴⁷. Some recent studies have shown that in organic molecular crystals hydrogen bonds often constitute the strongest intermolecular forces¹⁴⁸ and often dictate the preferred packing arrangement of the molecules^{149,150}. The enthalpies of hydrogen bond complex formation of cholesterol with aliphatic alcohols and triethylamine with aliphatic alcohols have been evaluated experimentally¹⁵¹. The intermolecular hydrogen bond lengths of $(\text{N-H}\cdots\text{N})^+$ and $(\text{O-H}\cdots\text{O})^-$ in a complex of 1,8-Bis(dimethylamino)naphthalene with Maleic Acid have been studied by X-Ray, Fourier-

transform Infrared, ^1H and ^{13}C Nuclear Magnetic Resonance¹⁵². The intermolecular hydrogen bond lengths are 2.606 Å for the (NHN) and 2.401 Å for the (OHO)⁺. Using calorimetric and IR spectroscopic methods, the values of thermodynamic functions of (1:1) hydrogen bond complex formation between cholesterol and some proton acceptors in CCl_4 have been determined¹⁵³. In an excellent study the Amide-Amide and Amide-Water hydrogen bonds have been studied and their implications on protein folding and stability established¹⁵⁴. FTIR spectroscopy has been used to investigate hydrogen bonding between alcohols, phenols and cholesterol with cyanate and azide anions in CCl_4 ¹⁵⁵. The cyanate and azide anions have been found to be the strongest hydrogen bond acceptors ever reported.

1.10 EMPIRICAL PARAMETERS OF SOLVENT POLARITY

A compilation of empirical parameters obtained by determining solvent dependent equilibrium constants, rate constants, absorption maxima (in the UV/Vis, IR, NMR or ESR region), or various other quantities and used to establish scales of solvent polarity is given in Table 4. A more detailed description of all the empirical solvent parameters known at present is given in a recent monograph¹⁵⁶.

Despite the already extensive number of 33 different solvent scales compiled in Table 4, only about six of them

(DN, Y, Z, $E_T(30)$, π^* and AN), known for a larger number of solvents or solvent mixtures, have so far found wider application in correlation of chemical reactivities. Particularly suitable standard compounds for the determination of empirical solvent parameters are solvatochromic dyes, because of measurement of absorption maxima of such dyes in solvents of different polarity is much easier to accomplish than the determination of rate or equilibrium constants of solvent dependent chemical reactions.

At present, the most comprehensive solvent scale is the $E_T(30)$ -scale, based on the transition energy for the solvatochromic intramolecular charge-transfer absorption of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio) phenolate:

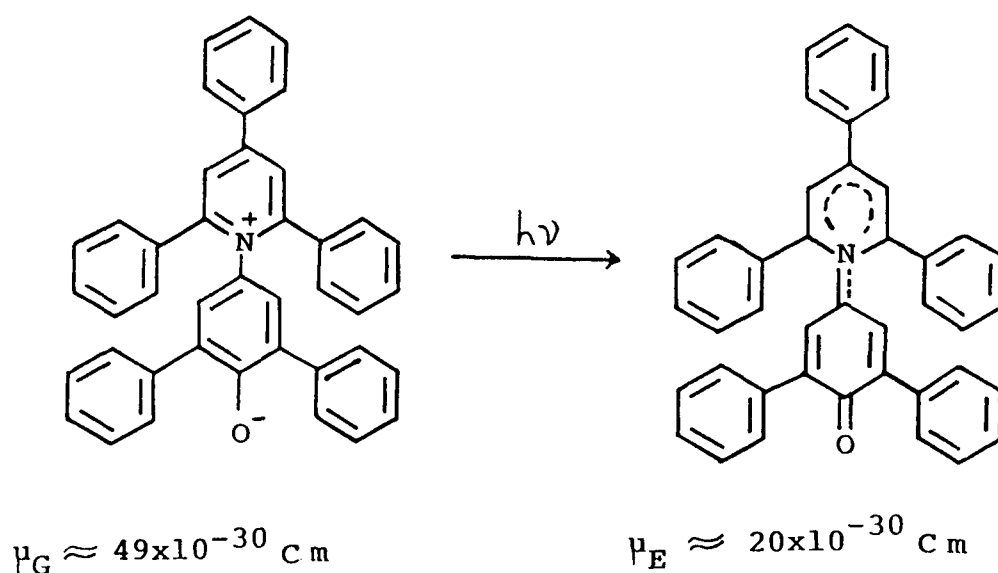


TABLE 4

EMPIRICAL PARAMETERS OF SOLVENT POLARITY

Symbol (name)	Physical quantity measured	Solvent-dependent standard process	Number of solvents	References
1	2	3	4	5
<u>From equilibrium measurements</u>				
(desmotropic constant)	equilibrium constant	diketo-enol tautomerism of ethyl acetoacetate at 20°C	13	157
$-\Delta G^{\circ}_{\text{OCH}_3}$	standard free energy	conformation equilibrium between cis-and trans-2- isopropyl-5-methoxy-1, 3-dioxane at 25°C	17	158
$-\Delta G^{\circ}$	standard free energy	NH/OH tautomerism equili- brium of Schiff bases of pyridoxal, 5'-phosphate at 25°C.	8	159
$\text{DN}(\text{donor number})$	reaction enthalpy - $\Delta H_{\text{EPD.SbCl}_5}$	1:1 adduct formation between antimony(V) chloride as standard-EPA and EPD-solvent in 1,2-dichloroethane at 25°C	45	160,161

1	2	3	4	5
<u>From measurements of reaction rates</u>				
Y(ionizing power, solvent electrophilicity)	relative rate constant k_1	S_N1 solvolysis of tert- butyl chloride at 25°C	11	162,163
N(solvent nucleophilicity)	relative rate constant k_2	S_N2 solvolysis of methyl bromide or methyl tosylate at 25°C		164-168
$\log k_1, \log k_{ion}, w$	rate constant k_1	solvolysis of 2-(4-methoxy- phenyl)-2-methylpropyl tosylate at 75°C	15	169
X	relative rate constant k_2	S_E2 reaction of tetramethyltin with bromine at 20°C	7	170,171
ρ ($\log k_2$)	rate constant k_2	S_N2 Menshutkin reaction between tri-n-propylamine and methyl iodide at 20°C	78	172,173
ρ	endo-/exo-product	Diels-Alder [$\pi^4_s + \pi^2_s$] cyclo- addition of cyclo- pentadiene to methyl acrylate at 30°C	14	174

1	2	3	4	5
<u>From UV/Vis spectroscopic measurements</u>				
Z	molar transition energy	charge-transfer absorption of 1-ethyl-4-methoxycarbonyl-pyridinium iodide at 25°C	88	60, 175-179
$E_T, E_T(30)$	molar transition energy	$\pi-\pi^*$ -absorption of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridiniophenolate at 25°C	207	156, 180-185
χ_R	molar transition energy	$\pi-\pi^*$ -absorption of a positively solvatochromic undecamethine cyanine dye at 25°C	58	186
χ_B	molar transition energy	$\pi-\pi^*$ -absorption of a negatively solvatochromic nonamethinenemrocyanine dye at 25°C	12	186
E_T, PM	molar transition energy	$\pi-\pi^*$ -absorption of 5-dimethyl-amino-2,4-pentadienal		187
$\bar{\nu}_1(F)$	wave number difference	n - π^* -absorption of saturated aliphatic ketones	23	188

1	2	3	4	5
E_K	molar transition energy	d- π^* -absorption of tetra-carbonyl [N-(2-pyridyl-methylene) benzylamino] molybdenum (0)	40	189
E_T^{SO}	molar transition energy	n- π^* -absorption of N,N-dimethylthiobenzamide S-oxide	35	190
$\alpha_{(\text{solvent HBD acidity})}$	wave number difference	$\pi-\pi^*$ -absorption of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenolate and 4-nitroanisole (1-methoxy-4-nitrobenzene), as well as further compounds	13	191,192
$\beta_{(\text{solvent HBA basicity})}$	wave number difference	$\pi-\pi^*$ -absorption of 4-nitro-aniline and N,N-diethyl-4-nitroaniline, as well as 4-nitrophenol and 4-nitroanisole	53	193-194

1	2	3	4	5
π^*	absorption wave number	p- π^* -and π - π^* -absorption of upto nine primary solvatochromic compounds, particularly nitrosubstituted arenes, as well as further compounds	95	195,196
<u>From IR spectroscopic measurements</u>				
G	relative wave number difference	IR stretching vibration absorption of X=O and X-H...B groups (X=C,S,N,O or P; B=HBA solvent) in the gas phase and in solution	20	197-198
B _{CH₃OD} (solvent Lewis basicity)	wave number difference	IR stretching vibration absorption of O-D in CH ₃ OD in the gas phase and in solution	55	199-200
B _{C₆H₅OH} (solvent Lewis basicity)	wave number difference	IR stretching vibration absorption of O-H in C ₆ H ₅ OH in the gas phase and in solution	198	201

1	2	3	4	5
<u>From ESR spectroscopic measurements</u>				
\mathcal{A}_N	\cdot splitting constant ^{14}N a	^{14}N -HFS splitting in the ESR spectra of three dialkylaminyloxy radicals	31	202, 203
<u>From NMR spectroscopic measurements</u>				
P	relative ^{19}F -NMR chemical shift	^{19}F -NMR absorption of 1-fluoro-4-nitrosobenzene	52	204, 205
AN (acceptor number)	relative ^{31}P -NMR chemical shift	^{31}P -NMR absorption of triethylphosphane oxide	46	206-208
<u>From miscellaneous measurements</u>				
S	equilibrium constant, rate constant, molar transition energy	mixed parameter, calculated from various solvent dependent processes, particularly from z-values	47	209
$\delta_{(\text{solubility parameter})}$	molar energy of vapourization, $E(=\text{molar cohesive energy}),$ and molar volume, $V_M,$ of the solvent	δ -values are the square roots of the molar cohesion energy densities, $\delta = (-E/V_M)^{1/2}$	ca. 400	210-213

1	2	3	4	5
I	difference of retention indices in gas-liquid chromatography	retention of selected standard compounds depending on the polarity of stationary liquid phases		214-217
P'	gas-liquid partition coefficients of selected standard solutes	distribution of different test-solutes (e.g. ethanol, 1,4-dioxane, and nitromethane)	75	216, 218-220
ξ^0 (eluant strength)	liquid-solid adsorption of solutes on alumina from different solvents	adsorption energy of solvent per unit area of adsorbent with unit activity in liquid-solid chromatography ($\xi^0=0$ for n-pentane on alumina)	46	220, 221

The $E_T(30)$ -value for a solvent is simply defined as the transition energy of the dissolved pyridinium-N-phenolate betaine dye measured in kcal/mol. A high $E_T(30)$ -value corresponds to high solvent polarity.

The $E_T(30)$ -values, now known for more than 200 solvents, provide a very useful empirical characterization of the solvent polarity owing to the exceptionally large displacement of the longest wavelength absorption band by solvents, reaching from 810 nm in diphenyl ether to 453 nm in water. Since the greater part of the solvatochromic range lies within the visible region of the electromagnetic spectrum, it is even possible to make visual estimation of solvent polarity by means of this betaine dye. In order to overcome solubility problems in nonpolar organic solvents, more lipophilic alkyl-substituted pyridinium-N-phenolates have been additionally used as secondary standard betaine dyes^{182,184}.

The use of a pyridinium-N-phenolate betaine dye as solvent polarity indicator follows from its following peculiar properties.

- (i) It exhibits a large permanent dipole moment of about 49×10^{-30} cm (ca. 15 Debye), suitable for the registration of dipole-dipole and dipole-induced dipole interactions.

- (ii) It possesses a large polarizable π -electron system, consisting of 44 π -electrons, suitable for the registration of dispersion interactions.
- (iii) With the phenolic oxygen atom it exhibits a highly basic electron pair donor (EPD) centre, suitable for hydrogen-bond interactions with protic solvents.

The positive charge of the cationic solvation centre is partially delocalized over the pyridinium ring and shielded by the phenyl substituents. Therefore, the $E_T(30)$ -values depend strongly on the electrophilic solvation power of the solvents, i.e. on their HBD ability or Lewis acidity, rather than on their nucleophilic solvation capability, for which the donor number of Gutmann, AN, is the better empirical solvent parameter.

The only limitation is that no $E_T(30)$ -values can be measured for acidic solvents such as carboxylic acids. Protonation at the phenolic oxygen atom of the betaine molecule leads to disappearance of the long wavelength solvatochromic absorption band. Since there exists a good linear correlation between $E_T(30)$ - and Z-values, the latter being measurable in acidic solvents, $E_T(30)$ -values can be calculated from the corresponding Z-values for such acidic solvents.

Some general features are suggested of the $E_T(30)$ scale. Solvents such as formamide ($\epsilon=111.0$) and N-methylformamide ($\epsilon=182.4$) which are considered as highly polar on account of their large dielectric constants, are by no means as polar as implied by their behaviour towards the betaine dye. N-Methylacetamide, the solvent with the highest dielectric constant ($\epsilon=191.3$), is in fact no more polar than ethanol.

Protic solvents always exhibit more polar behaviour towards the betaine dye than aprotic solvents of the same dielectric constant (e.g. 1-butanol and acetophenone). Steric effects cause protic solvents to become similar to aprotic ones and lead to decreasing $E_T(30)$ -values in a given solvent series (e.g. ethanol \longrightarrow 2-propanol \longrightarrow tert-butanol; phenol \longrightarrow 2-methylphenol \longrightarrow 2,6,-dimethylphenol).

According to their $E_T(30)$ -values, all the solvents studied may be divided roughly into three groups:

- (i) protic solvents (hydrogen bond donor or HBD solvents; $\epsilon > 15$, except carboxylic acids): $E_T(30)$ ca. 47 to 72.
- (ii) dipolar aprotic solvents (no HBD solvents: $\epsilon > 15$; $\mu > 8 \times 10^{-30}$ Cm: $E_T(30)$ ca. 40-47.
- (iii) apolar aprotic solvents (no HBD solvents; $\epsilon < 15$; $\mu < 8 \times 10^{-30}$ Cm: $E_T(30)$ ca. 30-40.

The classification is confirmed by other solvent characteristics.

The $E_T(30)$ -values of binary solvent mixtures are not related to their composition in a simple manner (Table 5). Addition of a small amount of a polar solvent to betaine solutions in nonpolar solvents causes a disproportionately large hypsochromic shift of the solvatochromic band indicating selective (or preferential) solvation of the dipolar betaine molecule by the more polar solvent¹⁸¹. In some binary solvent mixtures (e.g. trimethylphosphate/chloroform) a synergistic polarity effect causes larger $E_T(30)$ -values for the mixture than for the two components¹⁸⁵.

Spectroscopic solvent scales similar to the $E_T(30)$ -scale are the Z-scale⁶⁰ and the AN-scale^{206,207} both of which are also preferably measures of the electrophilic solvation power of the solvents.

Gutmann's acceptor number, AN, is defined according to equation 32 as the relative ^{31}P -NMR chemical shift of triethylphosphane oxide:

$$(\text{Et}_3\text{P}=\text{O} \leftrightarrow \text{Et}_3\text{P}^+ - \text{O}^-) + \text{EPA} \rightleftharpoons \text{Et}_3\text{P}^{\delta+} \cdots \text{O}^{\delta-} \rightarrow \text{EPA}$$

$$\text{AN} = \frac{\delta_{\text{corr}}}{\delta_{\text{corr}}(\text{Et}_3\text{PO}-\text{SbCl}_5)} \times 100 = \delta_{\text{corr}} \times 2.348 \quad \dots (32)$$

δ_{corr} the solvent dependent ^{31}P -NMR chemical shift of

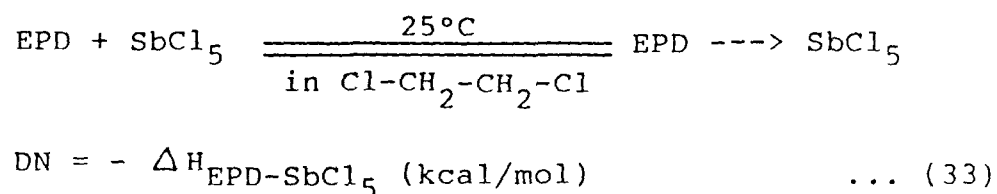
TABLE 5

EMPIRICAL PARAMETER OF SOLVENT POLARITY $E_T(30)$ kcal/mol, DERIVED FROM THE LONGEST-WAVELENGTH UV/VIS ABSORPTION BAND OF NEGATIVELY SOLVATOCHROMIC 2,6-DIPHENYL-4-(2,4,6-TRIPHENYL-1-PYRIDINIO) PHENOLATE, FOR NINE BINARY ORGANIC SOLVENT/WATER MIXTURES AT 25°C AND 1 BAR

Mixture ratio (V/V)solvent/ water	Organic solvent								
	Methanol	Ethanol	2-Propanol	Acetone	1,4-Dioxane	Pyridine	2-Methyl- pyridine	2,6-Dimethyl- pyridine	Piperidine
100:0	55.5	51.9	48.6	42.2	36.0	40.2	38.3	36.7	35.5
97.5:2.5	-	52.2	-	46.5	-	42.8	-	-	38.8
95:5	55.8	52.6	49.6	48.3	-	44.4	-	-	40.7
92.5:7.5	-	52.7	-	49.6	-	45.2	-	-	42.4
90:10	56.1	52.9	50.3	50.3	46.7	46.0	45.2	45.1	43.7
85:15	-	53.3	51.0	51.4	48.0	47.6	47.0	47.5	45.5
80:20	56.6	53.7	51.6	52.2	49.0	48.9	48.8	49.3	47.1
75:25	-	54.0	54.0	-	-	50.2	49.9	49.9	-
70:30	57.2	54.3	52.4	53.3	50.9	51.1	50.6	50.4	49.2
65:35	57.5	-	52.7	-	-	-	-	-	-
60:40	57.8	55.0	53.0	54.5	52.3	52.7	52.0	51.3	50.7
55:45	58.1	55.3	53.4	54.9	-	53.4	-	-	-
50:50	58.3	55.6	53.7	55.4	53.6	53.8	52.9	52.1	52.0
45:55	58.6	56.1	54.1	56.1	-	54.3	53.3	52.4	-
40:60	59.1	56.6	54.7	56.6	55.6	54.7	53.6	52.7	53.1
35:65	59.4	57.3	55.4	57.4	-	55.0	53.9	52.9	-
30:70	59.9	58.0	56.3	58.1	57.1	55.5	54.4	53.2	54.0
25:75	60.3	58.9	57.6	58.7	-	55.9	54.7	53.5	54.6
20:80	61.0	59.9	59.1	59.8	58.6	56.6	55.1	54.0	55.6
15:85	61.4	61.0	60.3	60.1	-	57.4	55.8	54.8	57.0
10:90	62.2	61.7	61.3	61.4	61.1	58.6	57.2	55.9	59.3
5:95	62.4	62.4	62.2	61.8	-	60.1	59.1	57.9	61.2
0:100	63.1	63.1	63.1	63.1	63.1	63.1	63.1	63.1	63.1

triethylphosphane oxide, extrapolated to infinite dilution, referred to n-hexane, and corrected for the difference between the volume susceptibilities of n-hexane and the solvent in question. The ^{31}P chemical shift of the 1:1 adduct, $\text{Et}_3\text{PO-SbCl}_5$, dissolved in 1,2-dichloroethane is used as the reference state; it is fixed arbitrarily as equal to 100. Accordingly, the dimensionless acceptor numbers vary from 0 (n-hexane) to 100 ($\text{Et}_3\text{PO-SbCl}_5$).

The use of solvent parameters to predict solvent effects should be limited in the first approximation to largely analogous processes (reactions, absorptions) since only then is the proportion of the different intermolecular forces in the solvent substrate interaction roughly the same as in the interaction between the solvent and the substrate used as reference compound. Hence the empirical donor numbers, DN, should be primarily a measure of the Lewis basicity or nucleophilicity of a solvent^{160,161}. They are defined, namely, as the negative enthalpies of the adduct formation between EPD solvents and antimony (V) chloride as the standard acceptor in a highly diluted 1,2-dichloroethane solution according to equation 33.



These donor numbers reflect the entire interaction of EPD solvents with the electron pair acceptor SbCl_5 , and are of particular significance in predicting coordination chemical reactions of metal cations in solution. The donor numbers vary from 0.1 kcal/mol for benzene to 61.0 kcal/mol for triethylamine.

The so called solvatochromic comparison method used by Kamlet and Taft for the introduction of three different but complementary solvent parameters deserves particular mention i.e. an α -scale of solvent hydrogen bond donor (HBD) acidities^{191,192}, a β -scale of solvent hydrogen-bond acceptor (HBA) basicities^{193,196,222} and a π^* -scale which denotes the combined solvent polarity polarizability effect (SPPE)¹⁹⁴⁻¹⁹⁶.

The β -values were derived from enhanced wave number shifts of 4-nitroaniline relative to its homomorph N,N-diethyl-4-nitroaniline, and 4-nitrophenol relative to 4-nitroanisole, both pairs of standard compounds measured in a series of HBD and HBA solvents. All four standard compounds are capable of acting as H-bond acceptors (via the oxygen atoms in the nitro group) in HBD solvents, but only 4-nitroaniline and 4-nitrophenol can also act as H-bond donors in HBA solvents (via the amino and hydroxy group, respectively). Taking the $\Delta\Delta\bar{\nu}$ -value of 2800 cm^{-1} measured for 4-nitroaniline/N,N-diethyl-4-nitroaniline in

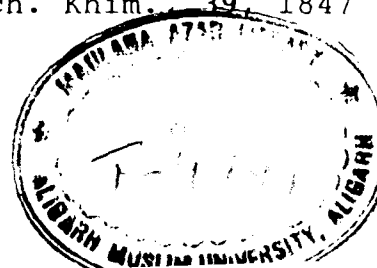
hexamethylphosphoric acid triamide (a particularly strong HBA solvent) as a reference point ($\beta_2 = 1.000$, it was at last possible to obtain a solvent β -scale for HBA or Lewis basicities for 53 HBA solvents.

By basically the same method, using the enhanced solvatochromic shifts for Dimroth-Reichardt's pyridinium-N-phenolate betaine (and other related compounds) relative to 4-nitroanisole, an α -scale of the HBD or Lewis acidities for 13 HBD solvents was established by Kamlet and Taft, taking the $\Delta\bar{\nu}$ -value of 6240 cm^{-1} measured for the betaine/4-nitroanisole pair in methanol (a strong HBD solvent) as reference point ($\alpha_1 = 1.000$). Whereas the betaine dye can act as a strong H-bond acceptor (via the phenolate oxygen atom), the corresponding 4-nitroanisole cannot.

Finally, a π^* -scale of solvent polarity-polarizability was established by Kamlet and Taft, based on solvent effects of upto nine primary standard compounds, particularly nitroaromatics, which had been selected in order to minimize hydrogen-bond effects between standard compounds and solvents. Using $\pi^* = 0.000$ for cyclohexane and $\pi^* = 1.000$ for dimethyl sulfoxide as reference points, and using the correlations of primary π^* -values with additional solvent-dependent processes, a π^* -scale for 95 solvents has been constructed).

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CHAPTER - 2

ISOLATION OF CHARGE TRANSFER BANDS OF SOME POLYNITRO- AROMATIC-DIPHENYLAMINE SYSTEMS

INTRODUCTION

Some workers^{1,2} have studied the interaction of dinitrobenzenes with anilines but could not satisfactorily isolate the charge-transfer bands in these systems.

The reasons could be manifold. Since the complexes are weak, the bands may not be observed due to 'local excitations' in the donor, the acceptor or both, or the band may be so close to the absorption of a component so that it is masked. It is also possible that the complex be so weak that though colour formation takes place it may not warrant a separate absorption.

In the systems I have studied the main cause is the large absorption showed by polynitroaromatics in the region of the charge-transfer bands.

Using a simple technique we have satisfactorily isolated the charge-transfer bands of polynitroaromatics-aromatic amine (diphenylamine) systems.

EXPERIMENTAL

Diphenylamine (BDH Analar), nitrobenzene (Pfizer), o-dinitrobenzene (BDH), m-dinitrobenzene (BDH Analar), p-dinitrobenzene (BDH Analar), 1-chloro-2,4-dinitrobenzene (E. Merck G.R.), 3,5-dinitrobenzoic acid (E. Merck, G.R.), and 2,4-dinitrotoluene (Fluka G.R.) were used. The G.R. and Analar reagents were used as received. Other reagents were recrystallised till their melting points were in agreement with reported values. Carbon tetrachloride and ethyl

alcohol were used as solvents. All measurements were carried out on Bausch and Lomb spectronic 1001 uv-visible spectrophotometer. The association constants were evaluated under the condition that the donor concentration was kept in far excess over the acceptor concentration.

RESULTS AND DISCUSSION

Since polynitroaromatics absorb strongly in the region of interest the spectra were recorded by taking an equal concentration of the polynitroaromatics both in the reference and the sample cell. Diphenylamine did not absorb in the region of interest.

Figures 1-7 give the charge-transfer spectra for the various polynitroaromatic-diphenylamine complexes. As expected for weak molecular complexes they are broad featureless bands. These charge-transfer bands of dinitrobenzenes and diphenylamine are perhaps being reported for the first time.

Figure 8 shows the expected dependence of $\bar{\nu}_{CT}$ on electron affinity. The electron affinities of o-, p- and m-dinitrobenzenes are known. A plot of electron affinities of these dinitrobenzenes against $\bar{\nu}_{CT}$ gives a straight line. The electron affinities of some other dinitrobenzenes

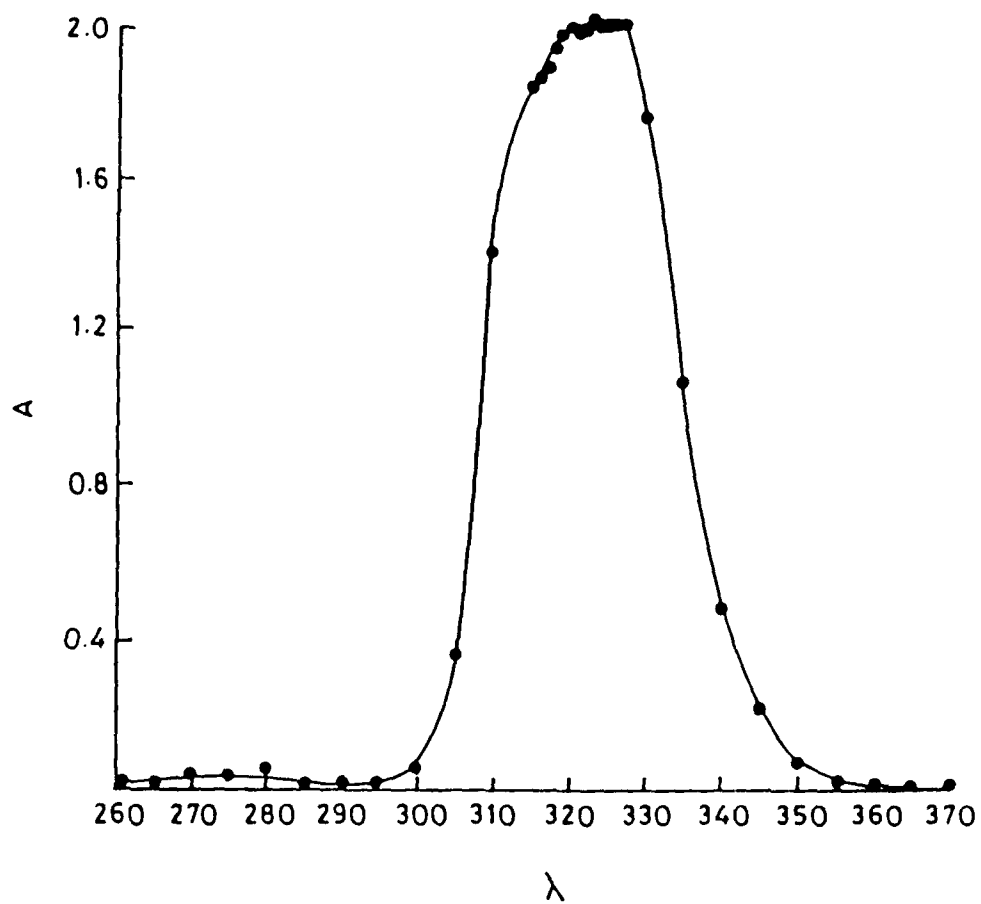


Fig. 1 Charge-transfer band for the Nitrobenzene-Diphenylamine system in CCl_4 . λ_{max} found 320 nm.

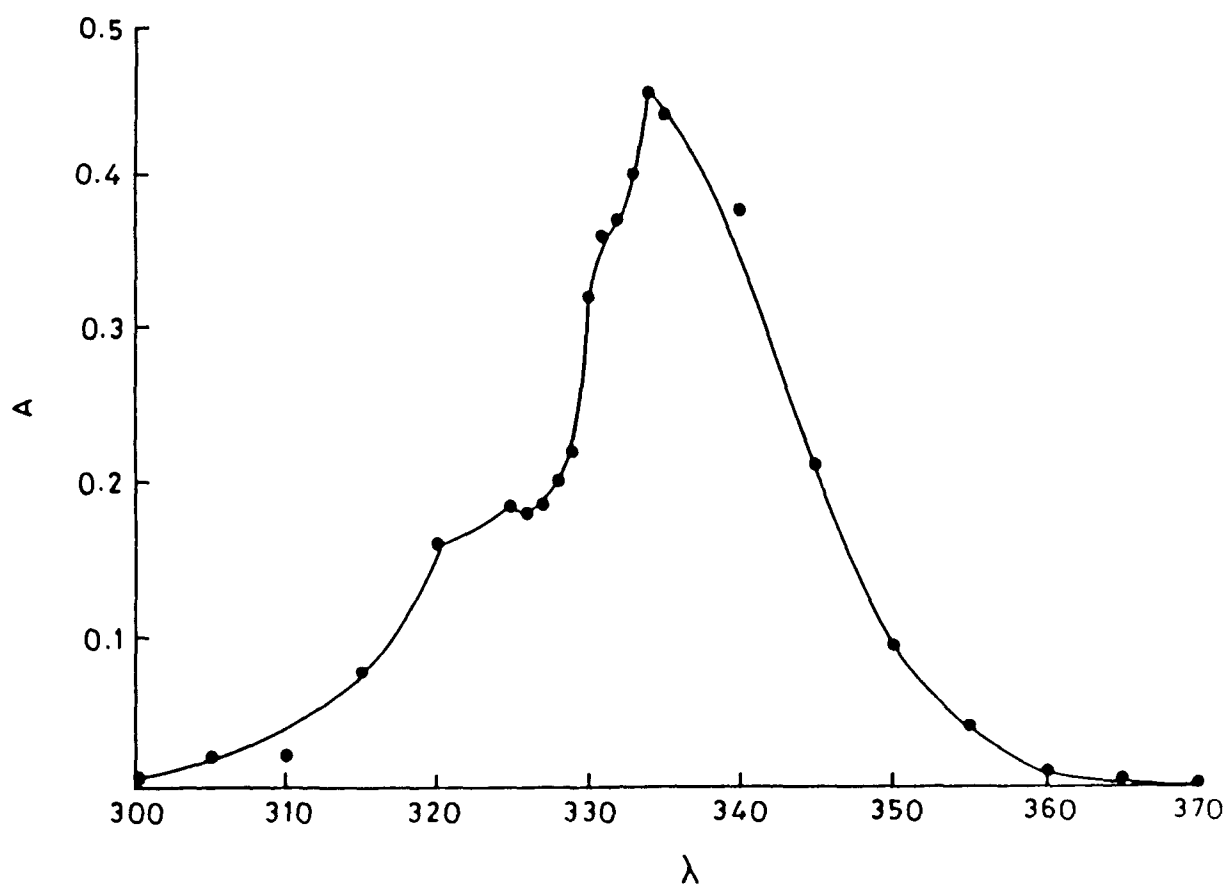


Fig. 2 Charge-transfer band for the o-dinitrobenzene-Diphenylamine system in CCl_4 . λ_{max} found 334 nm.

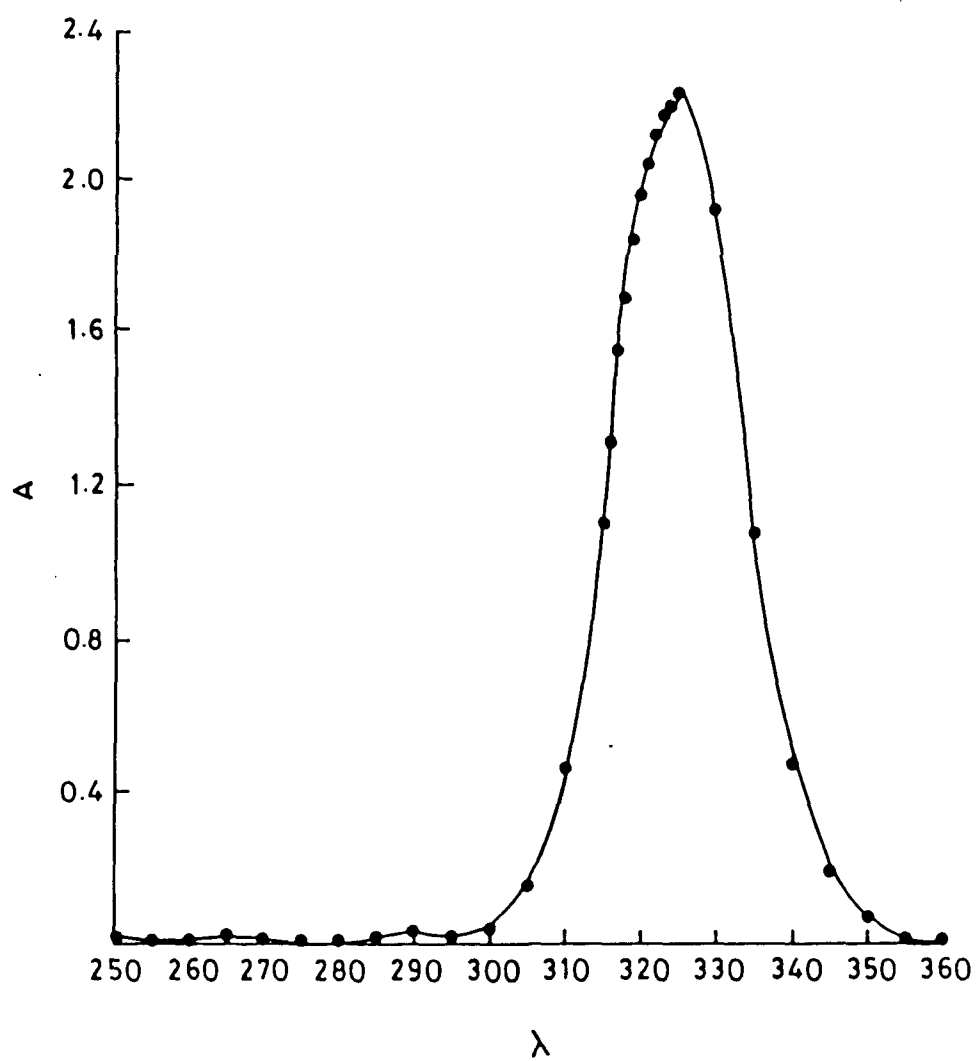


Fig. 3 Charge-transfer band for the m-dinitrobenzene-diphenylamine system in CCl_4 . λ_{max} found 325 nm.

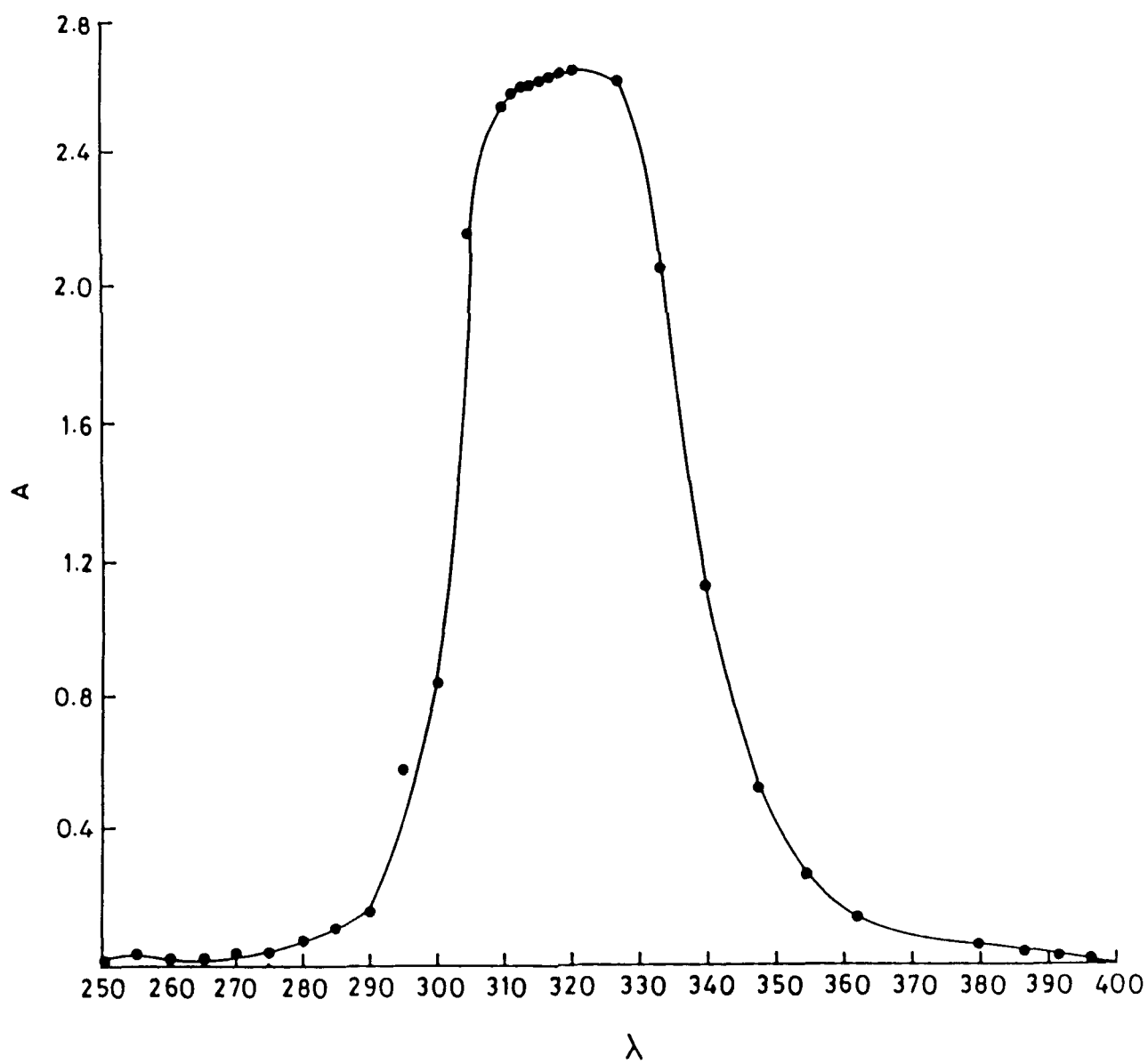


Fig. 4 Charge-transfer band for the p-dinitrobenzene-diphenylamine system in CCl_4 . λ_{max} found 320 nm.

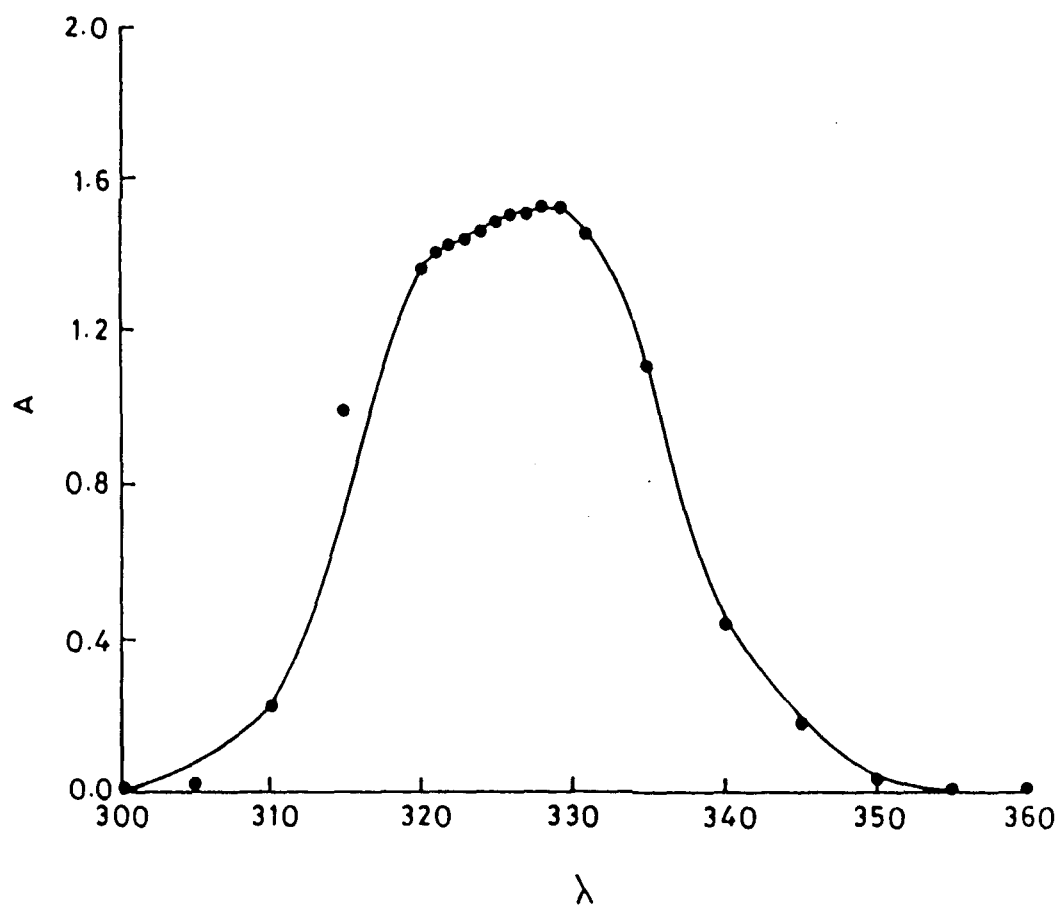


Fig. 5 Charge-transfer band for the 1-chloro-2,4-dinitrobenzene-diphenylamine system in CCl_4 . λ_{max} found 328 nm.

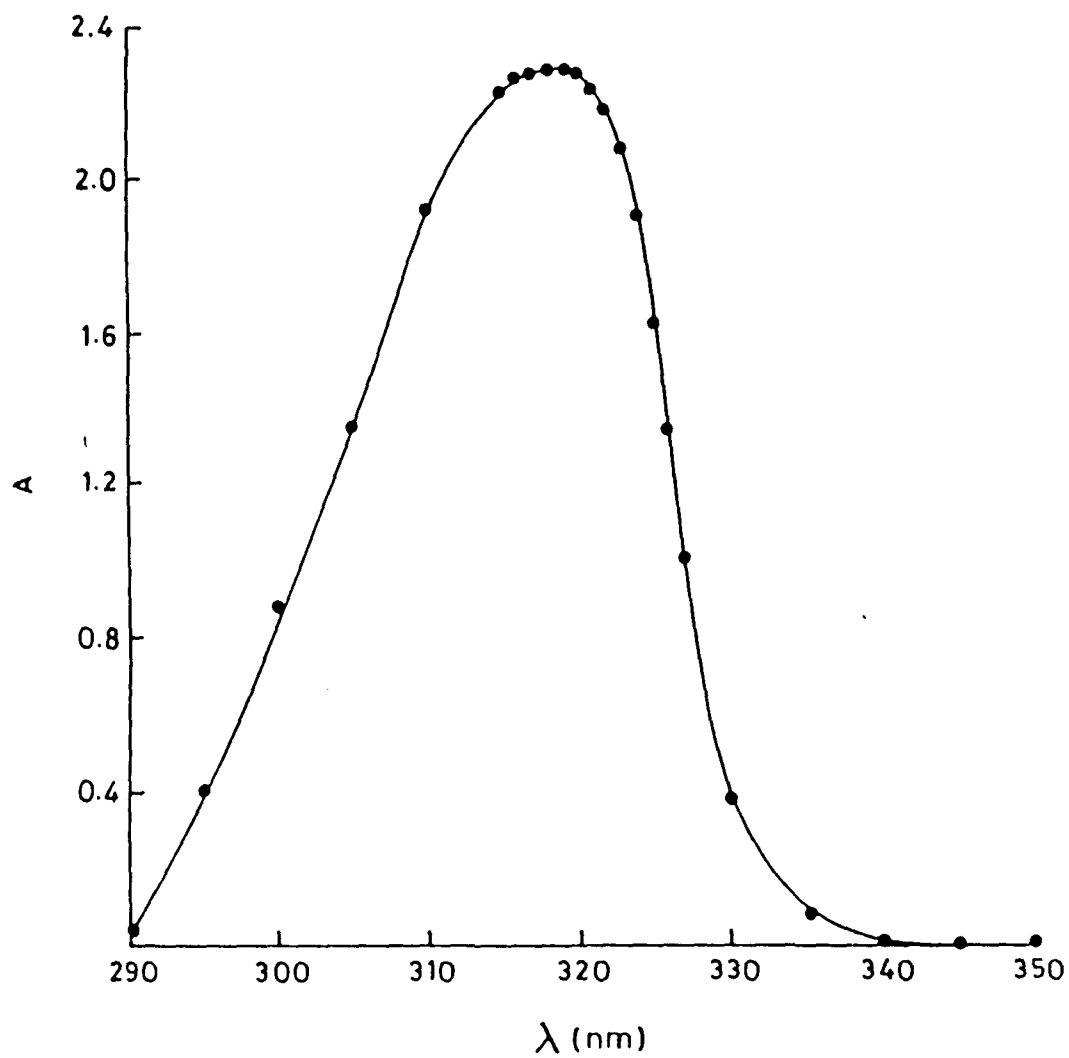


Fig. 6 Charge-transfer band for the 3,5-dinitrobenzoic acid-diphenylamine system in ethanol. λ_{max} found 318 nm.

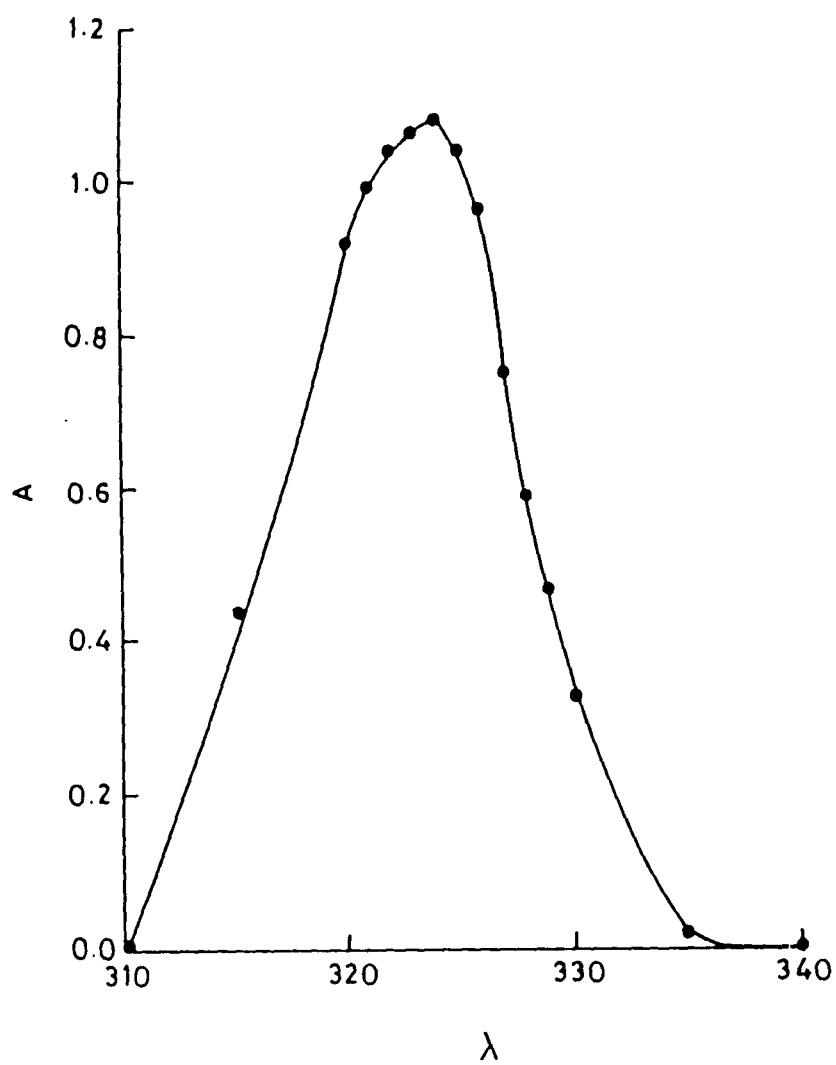


Fig. 7 Charge-transfer band for the 2,4-dinitro-
toluene - diphenylamine system in CCl_4 .
 λ_{max} 324 nm.

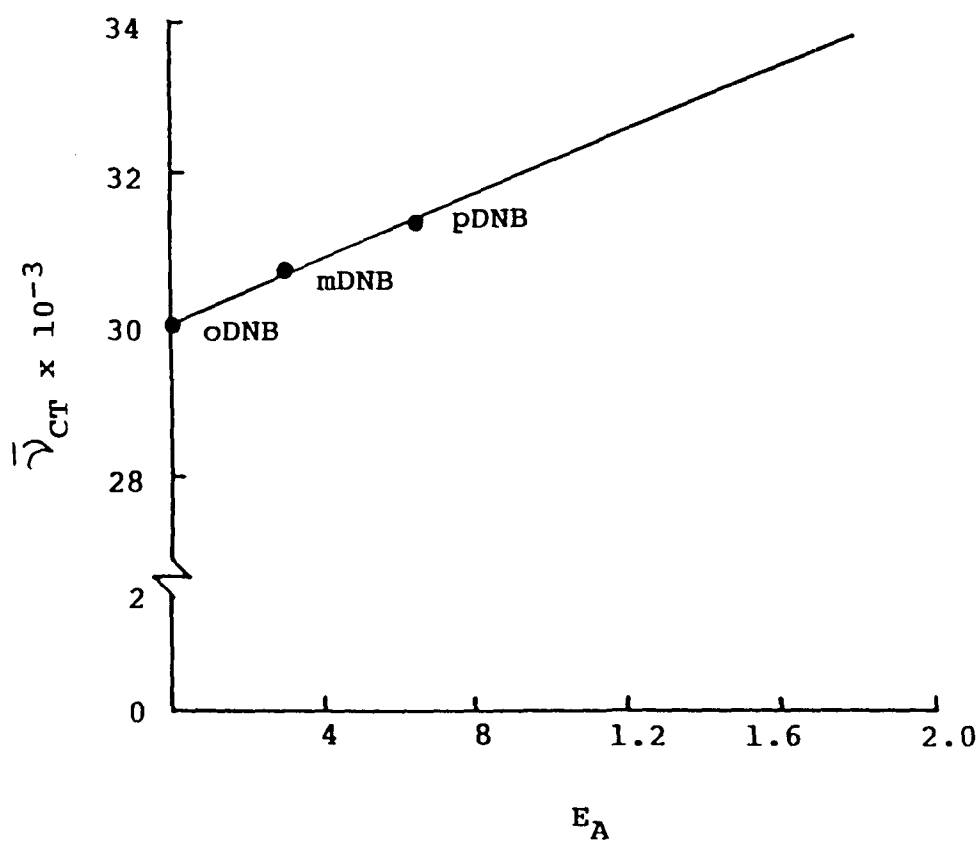


Fig. 8 A plot of $\bar{\gamma}_{CT}$ for the o-, m-, and p-dinitrobenzene complexes to diphenylamine and electron affinities of the dinitrobenzenes.

(not known till date) have been evaluated from their respective charge-transfer bands and are given in Table 1.

Since polynitroaromatics absorb strongly at their charge-transfer maxima, a compensation procedure first proposed by Mulliken³ may produce an optically silent detector. Therefore, charge-transfer bands alone may not establish charge-transfer in these systems but may have to be complemented with an independent data. We have already shown previously (Figure 8) that there is a linear relation between $\bar{\nu}_{CT}$ and electron affinities of those acceptors which are available, this also is indicative of charge transfer. Table 2 reports the association constants of the complexes which show the expected range for similar types of complexes (see inset Table 2).

Equilibrium constant measurements were carried out at 400 nm where the polynitroaromatics do not absorb and the above difficulties do not, therefore, arise. The equation used was, the well known Benesi-Hildebrand equation⁴

$$\frac{[A]_0}{A} = \frac{1}{K \epsilon_{400}} \frac{1}{[D]_0} + \frac{1}{\epsilon_{400}} \quad \dots (1)$$

under the condition $[D]_0 \gg [A]_0$. $[D]_0$ in equation 1 signifies the initial concentration of donor (diphenylamine). $[A]_0$ as initial concentration of acceptor

TABLE 1

INFERRED ELECTRON AFFINITIES FROM CHARGE-TRANSFER
BANDS

Nitroaromatic compound	Electron Affinity
2,4-Dinitrotoluene	0.64
1-Chloro-2,4-dinitrobenzene	0.90
Nitrobenzene	0.50
3,5-Dinitrobenzoicacid	0.68

(dinitroaromatic compound) and A is the absorbance of the complex. $[A]_0$ was fixed constant (.01 M) in all the solutions while $[D]_0$ was varied (.1, .2, .3, .4 M). A plot of $[A]_0/A$ vs $1/[D]_0$ is linear with the slope equal to $1/K \epsilon_{400}$ and the intercept $1/\epsilon_{400}$. The association constant K is then obtained by dividing the intercept by the slope.

The trend of data in Table 2 further confirms the charge-transfer chemistry of these complexes. Nitrobenzene which has only one nitro group can only be a very weak acceptor and so is 2,4-dinitrotoluene which contains a methyl donor group and hence these two have the lowest values of K . o-Dinitrobenzene even though having two nitro groups is again a weak acceptor (electron affinity zero). m-Dinitrobenzene is a moderately good acceptor and hence has a higher value of K . The slightly higher value of K of the 1-chloro-2,4-dinitrobenzene complex over that of m-dinitrobenzene complex is due to the electron withdrawing nature of -Cl in the former giving it a higher acidity than m-dinitrobenzene. The value for p-dinitrobenzene complex is as expected as it is a strong acceptor than m-dinitrobenzene. The highest K obtained for this series is for 3,5-dinitrobenzoic acid. This is perhaps due to the presence of a permanent charged acidic group in addition to two nitro

groups. This enhances the acidity of the molecule to an extent that it forms the strongest complex (in the present series).

TABLE 2

EQUILIBRIUM CONSTANTS OF SOME DINITROAROMATIC-DIPHENYLAMINE COMPLEXES

Complex	K (litre mole ⁻¹)	Complex	K
3,5-Dinitrobenzoic acid-DPA	1.56	pDAB-DNT ¹	3.90
1-Chloro-2,4-dinitrobenzene-DPA	1.40	Ind-DNT ²	0.93
p-Dinitrobenzene-DPA	1.34		
m-Dinitrobenzene-DPA	1.225		
Nitrobenzene-DPA	0.80	1. P.M. Qureshi, S.B. Singh and A. Mohammad; J. Solid State Chem. 81, 230 (1989).	
2,4-dinitrotoluene-DPA	0.80	2. R.K. Varshney; Ph.D. Thesis, Aligarh Muslim University, Aligarh, India (1989).	
o-Dinitrobenzene-DPA	0.15		

DPA = Diphenylamine
 pDAB = p-Dimethylaminobenzaldehyde
 Ind = Indole
 DNT = 2,4-Dinitrotoluene

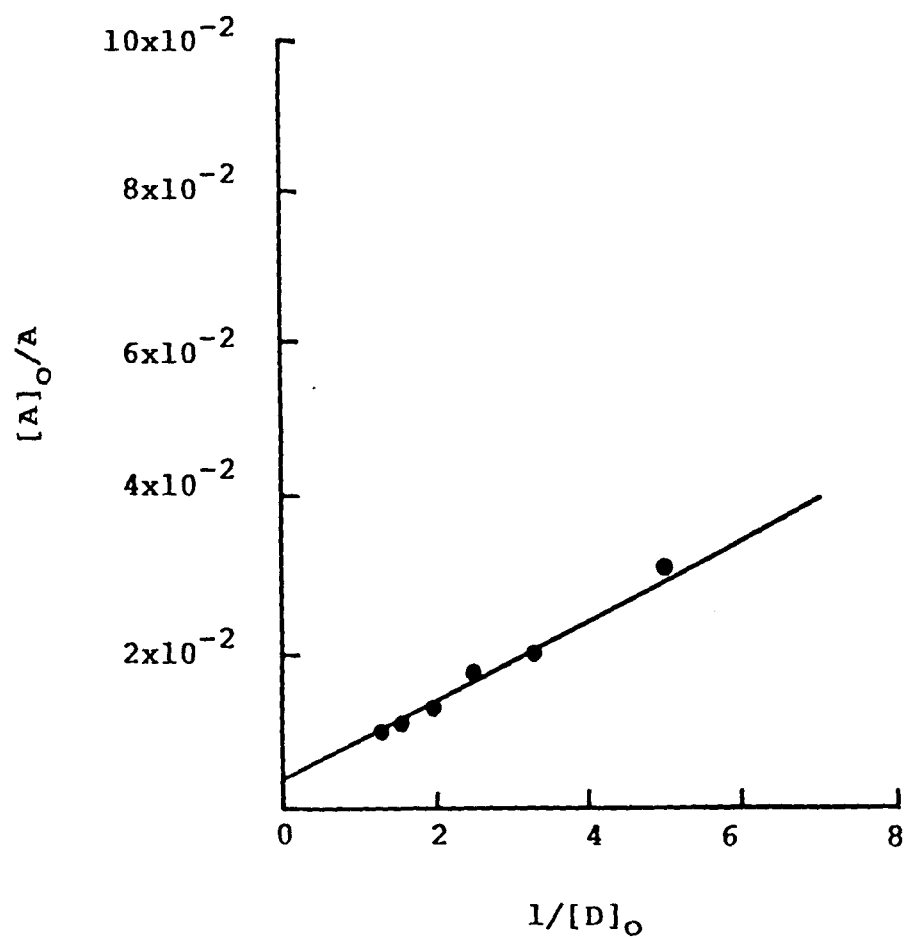


Fig. 9 Benesi-Hildebrand plot for the nitrobenzene-diphenylamine system in CCl_4 at 440 nm.

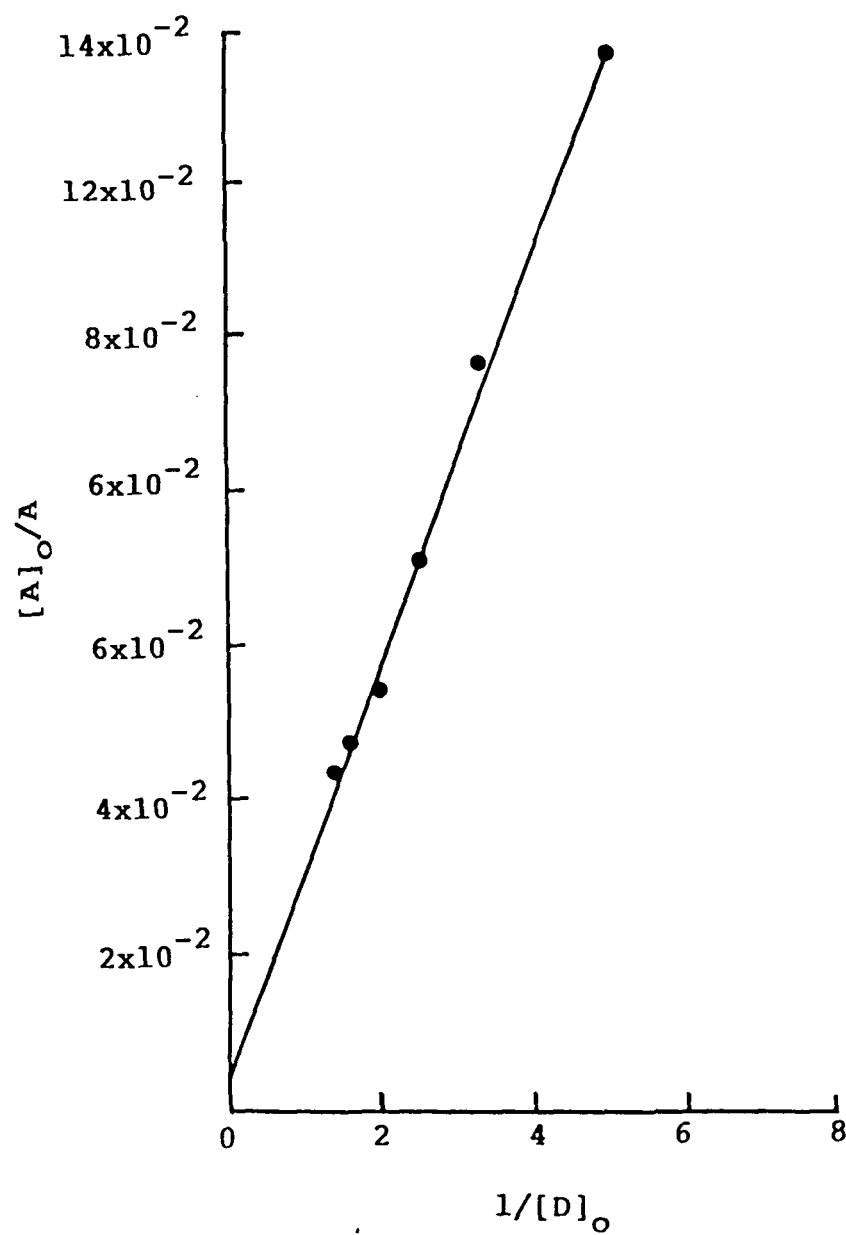


Fig. 10 Benesi-Hildebrand plot for the o-dinitrobenzene-diphenylamine system in CCl_4 at 400 nm.

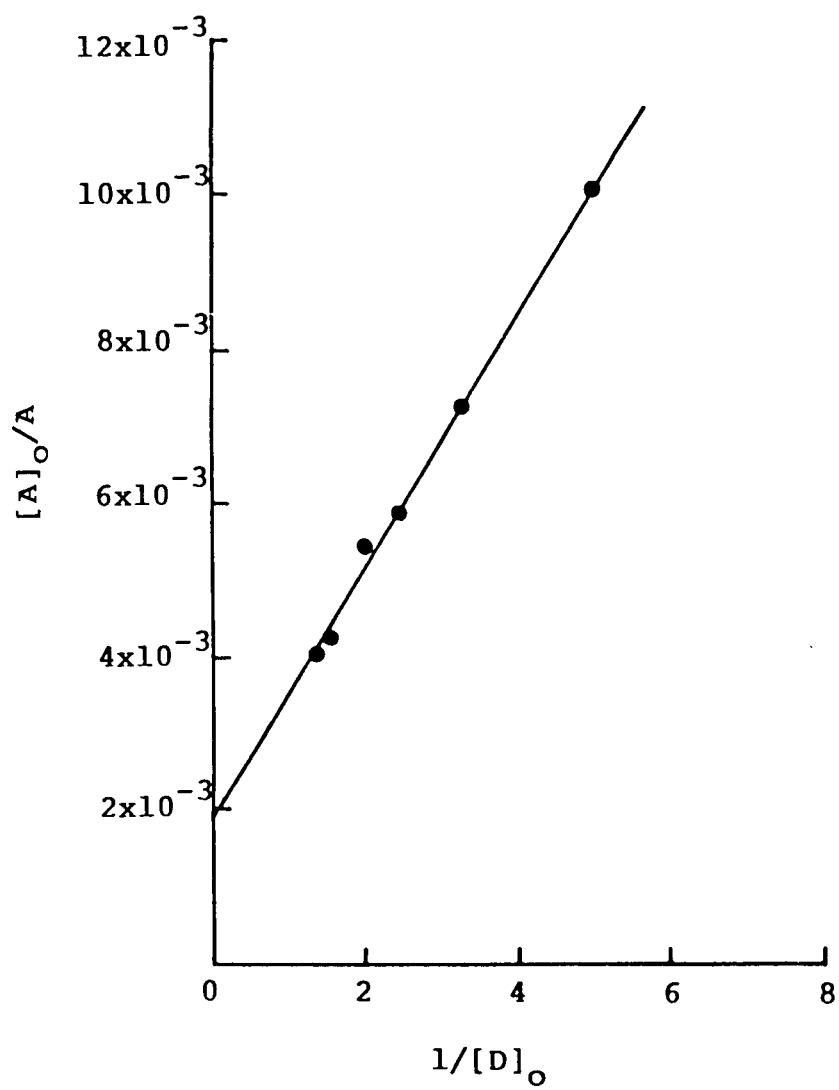


Fig. 11 Benesi - Hildebrand plot for the m-dinitrobenzene-diphenylamine system in CCl_4 at 400 nm.

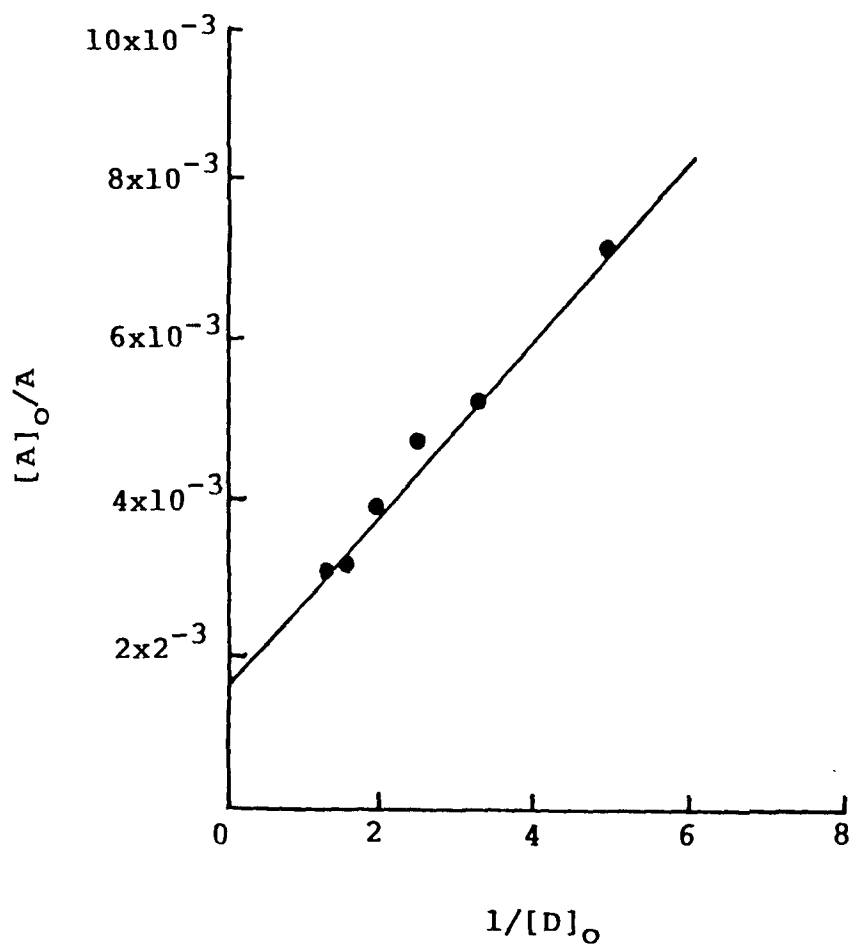


Fig. 12 Benesi-Hildebrand plot for the p-dinitrobenzene-diphenylamine system in CCl_4 at 400 nm.

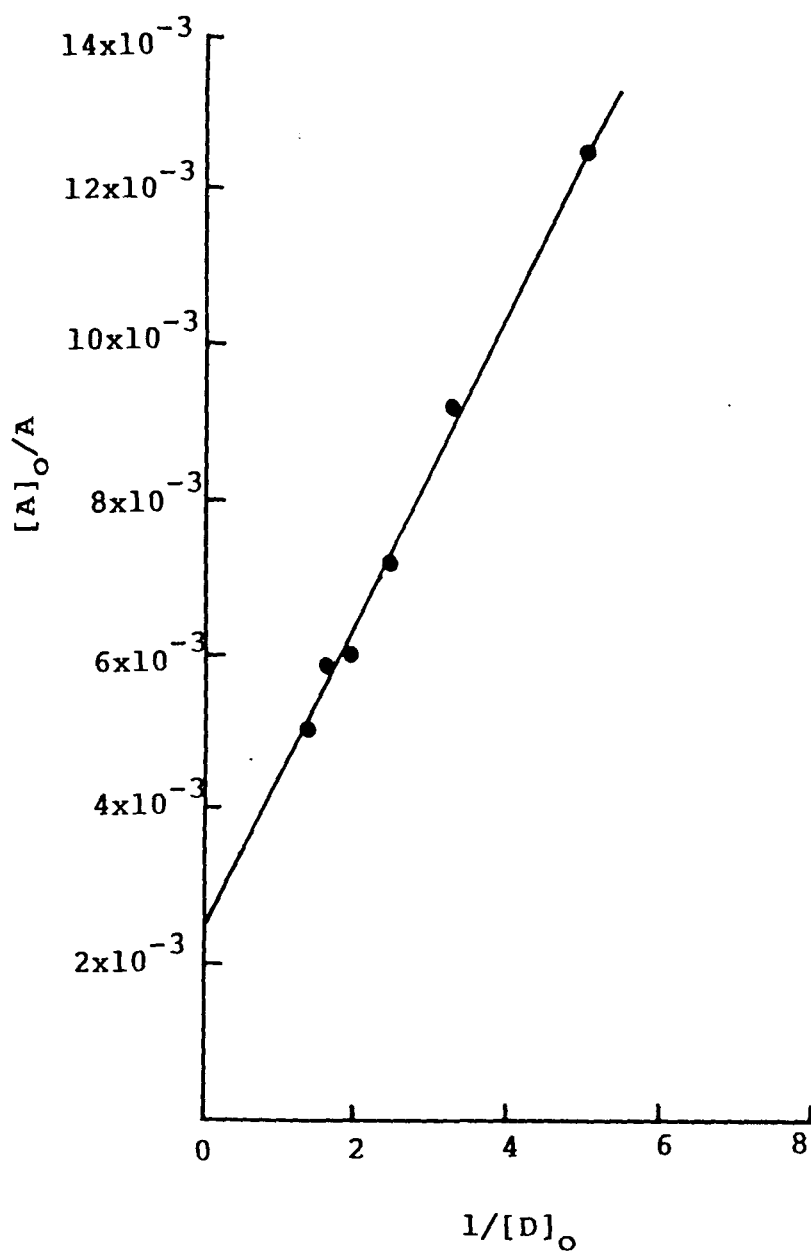


Fig. 13 Benesi-Hildebrand plot for the 1-chloro-2,4-dinitrobenzene-diphenylamine system in CCl_4 at 400 nm.

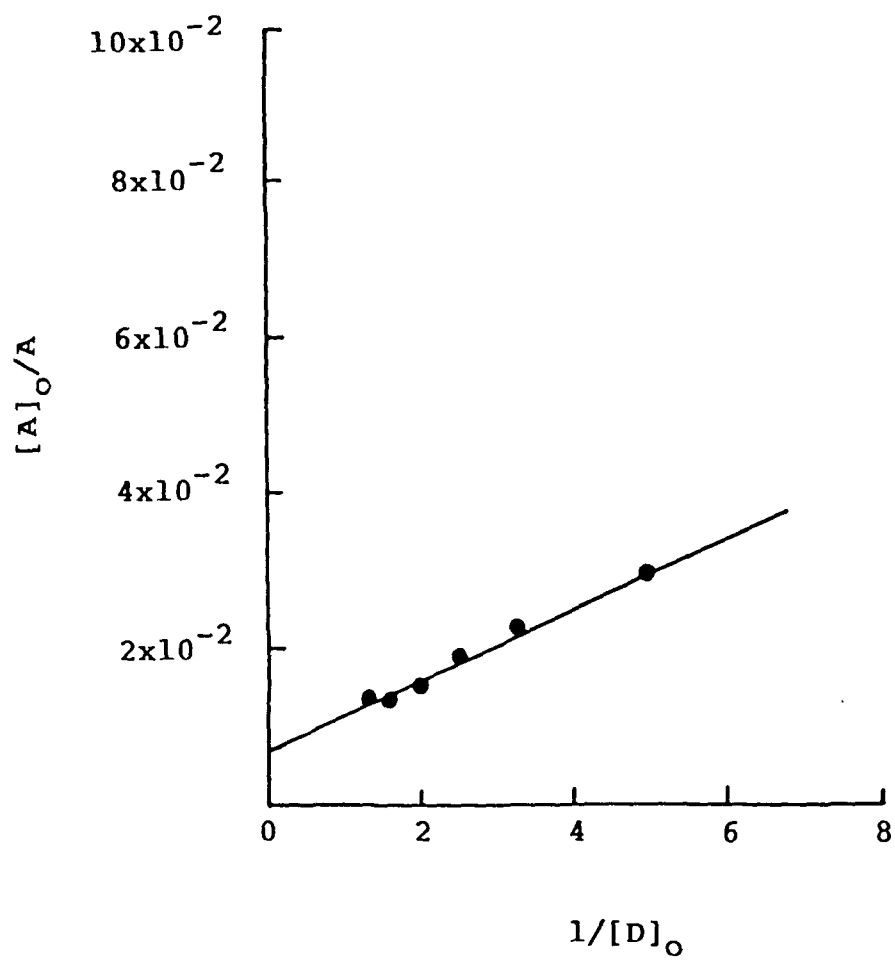


Fig. 14 Benesi-Hildebrand plot for the 3,5-dinitrobenzoic acid-diphenylamine system in ethanol at 400 nm.

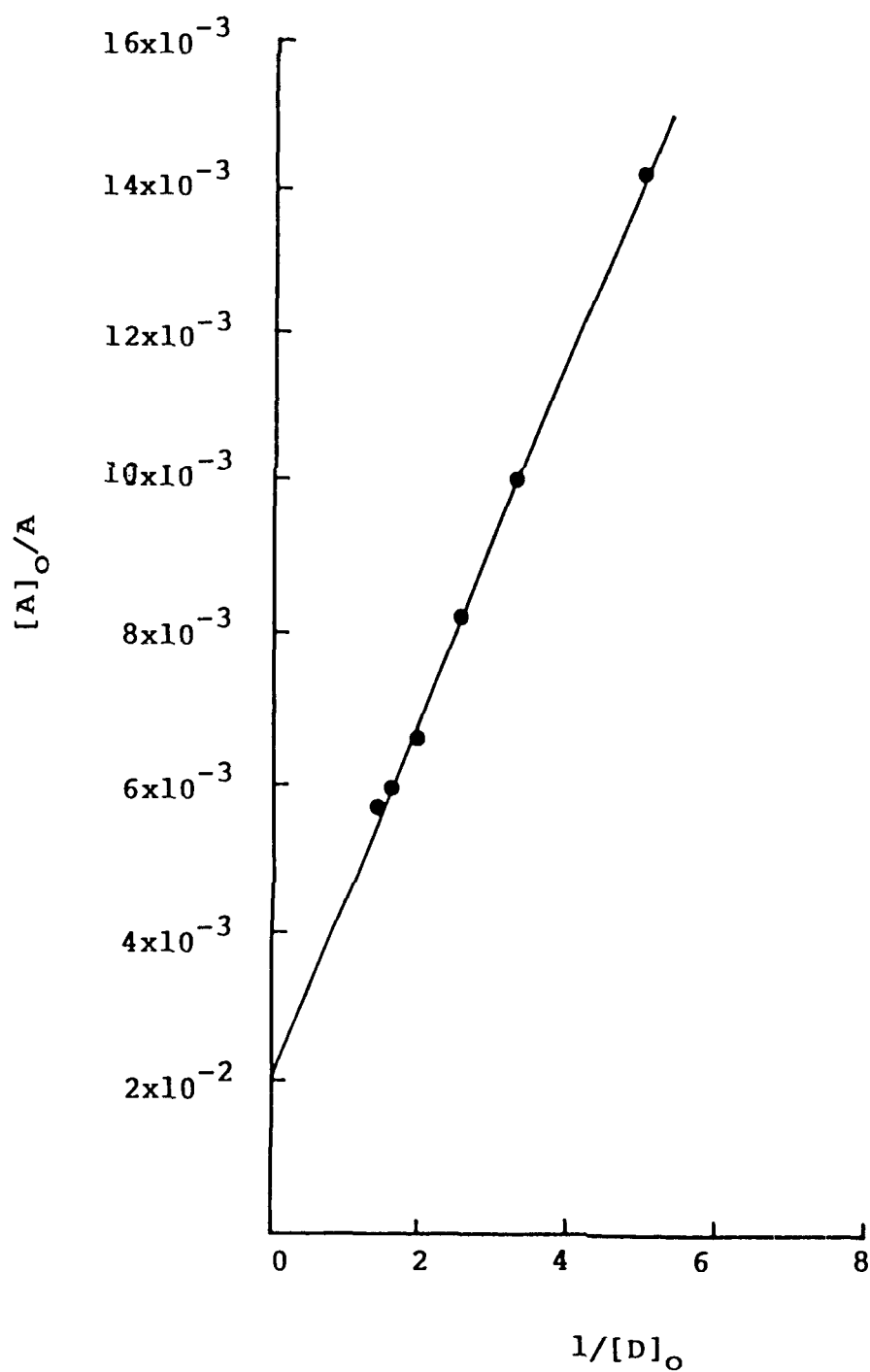


Fig. 15 Benesi-Hildebrand plot for the 2,4-dinitrotoluene-diphenylamine system in CCl_4 at 400 nm.

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INTRODUCTION

The π^* -scale was first devised for non hydrogen bond donor solvents¹. However, surprisingly no simple linear correlation has been found between $E_T(30)$ and π^* -values. Restriction of the solvatochromatic comparison to only those solvent sets which have common structural features gives separate correlation lines for different families of solvents¹. Recent studies show several deficiencies in the manner in which the π^* -scale was devised. These are summarised². No mention is made however of α -scale³. The α -scale was devised to get a linear fit between XYZ (usually a spectroscopic parameter) $a\alpha$ and $s\pi^*$. However, the α -scale has been criticized extensively⁴. A new solvent polarity parameter ϕ that correlates linearly to π^* without recourse to α is proposed here.

EXPERIMENTAL

2,4-Dinitrotoluene (DNT) was an AR reagent from E. Merck, Darmstadt, Diphenylamine (DPA) was an AR reagent from BDH, Poole England, and were used as received. All solvents were AR grade and also received as used. The 2,4-Dinitrotoluene-Diphenylamine complex has been well characterised as a charge-transfer complex⁵ in CCl_4 . Since the association constant is only 0.23 l mol^{-1} , it implies that there is no likelihood of ion formation taking place

even in polar solvents. Therefore, the position of equilibrium will be indicative of the solvent polarity. Equilibrium constants were determined by optical spectroscopy using the Benesi-Hildebrand equation⁶.

$$\frac{[A]_0}{A} = \frac{1}{K \epsilon_{400}} \cdot \frac{1}{[D]_0} + \frac{1}{\epsilon_{400}}$$

where $[A]_0$ is the initial concentration of acceptor, $[D]_0$ is the initial concentration of donor and K is the equilibrium constant. A and ϵ_{400} are the absorbance and the molar absorptivity of the complex at 400 nm. 400 nm was selected because the absorption of free DNT may be cancelled by taking equal concentration of free DNT in the reference cell⁷. At higher wavelengths the nitro compounds absorb strongly and compensation is not satisfactory. A plot of $[A]_0/A$ vs $1/[D]_0$ under the condition $[D]_0 \gg [A]_0$ is linear. ϵ_{400} is obtained from the intercept and K from the slope. The measured K does not show a wavelength dependence. K has been determined in 11 hydrogen bond donor solvents given in Table I.

RESULTS AND DISCUSSION

The 15 years of π^{*2} have seen phenomenal rise in the importance and uses of this scale. However, it does not correlate linearly to the more comprehensive $E_T(30)$ scale. While $E_T(30)$ scale is based on the overall solvation of the

15 YEARS OF π^* AND THE ρ -SCALE

CHAPTER - 3

pyridinium-N-phenolate betaine, the nitroaromatics are used for the π^* -scale. The π^* scale is based on relationships of the type.

$$XYZ = XYZ_0 + a\alpha + b\beta + SPPE \quad \dots (1)$$

where XYZ is some parameter (here a spectroscopic parameter), SPPE denotes the solvent polarizability effect, α and β are hydrogen bond donor and acceptor properties respectively. a and b are variable parameters. Equation 1 approximates to

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \quad \dots (2)$$

Recently the above method has been criticized on several grounds², namely

- (1) The need for averaging a no. of indicators.
- (2) π^* values are indicator dependent^{9,10}.
- (3) The difference between $E_T(30)$ and π^* lies in different responses to respective indicator.
- (4) The solvatochromic band of N,N-diethyl-4-nitroaniline (the single most widely used indicator) has a significant vibrational structure leading to a solvent dependent band shape¹¹.
- (5) The combination of data for solvatochromic indicators in supercritical fluids raise intriguing questions when combined with the gas phase results.

Another deficiency (as mentioned earlier) is the applicability of the π^* -scale to hydrogen bond donor solvents. In this direction the π^* -scale depends heavily on the α scale.

It follows from equation 2

$$XYZ = s\pi^* + a\alpha + XYZ_0 \quad \dots (3)$$

since for hydrogen bond donor solvents $\beta = 0$

Unfortunately 15 years of π^* -scale does not reflect on this important problem. This is because when non-hydrogen bond donor solvents are compared no such simple relation exists. Equation 3 implies a three dimensional plot between XYZ, $s\pi^*$ and $a\alpha$. This has been recently used to set up equations like¹².

$$\Delta E_{\max}^* = 10.465 \pi^* + 10.544\alpha + 43.437 \quad \dots (4)$$

$$\Delta E_{\max}^f = 3.304 \pi^* + 4.178\alpha + 47.032 \quad \dots (5)$$

where ΔE_{\max}^* and ΔE_{\max}^f are absorption and fluorescence energies for a typical merocyanine dye.

Where the significance of α is concerned, it suffers from several disadvantages⁴. First of all it is restricted to closely related families of solvents. Secondly, the values are in error for aromatic hydrogen bond donor solvents. Moreover, in many cases there is an incorrect rankings of α values and the complication caused

by competing self association has introduced serious uncertainties in the determination and use of solvent α values. Therefore, a need was felt to develop an independent solvent polarity parameter which is linear with π^* and independent of α . Such a parameter $\bar{\phi}$ is defined here $\bar{\phi}$ is applicable to strong and weak hydrogen bond donor solvents. $\bar{\phi}$ takes the definition

$$\bar{\phi} = \ln K$$

where K is the equilibrium constant of the 2,4-Dinitro-toluene-Diphenylamine complex in various solvents.

It is readily seen that there is a near exact linear relationship between $\bar{\phi}$ and π^* (Figure 1). This relationship obviates the need for α and $\bar{\phi}$ directly measures the solvent hydrogen bond donor strength. Other solvent polarity parameters like Z (Figure 2)¹³, AN (Figure 3)¹⁴ and $E_T(30)$ (Figure 4)¹⁵ which do not correlate linearly with π^* obviously do not correlate with $\bar{\phi}$. Therefore, $\bar{\phi}$ becomes perhaps the first solvent polarity parameter to correlate linearly with π^* for a series of hydrogen bond donor solvents.

TABLE 1

VALUE OF EQUILIBRIUM CONSTANT K OF DINITROTOLUENE-DIPHENYLAMINE COMPLEX AND ϕ ($= \ln K$) IN DIFFERENT SOLVENTS

S.No.	Solvent	K(DNT-DPA CT complex in CCl_4)	ϕ ($= \ln K$)
1	t-Butanol	0.25	-1.39
2	l-Butanol	0.314	-1.14
3	2-Propanol	0.45	-0.80
4	Acetic acid	0.50	-0.70
5	l-Propanol	0.54	-0.68
6	Ethanol	0.69	-0.37
7	Chloroform	0.76	-0.27
8	Methanol	0.80	-0.22
9	Acetone	2.00	0.69
10	Ethylene glycol	4.82	1.57
11	Formamide	8.88	2.18

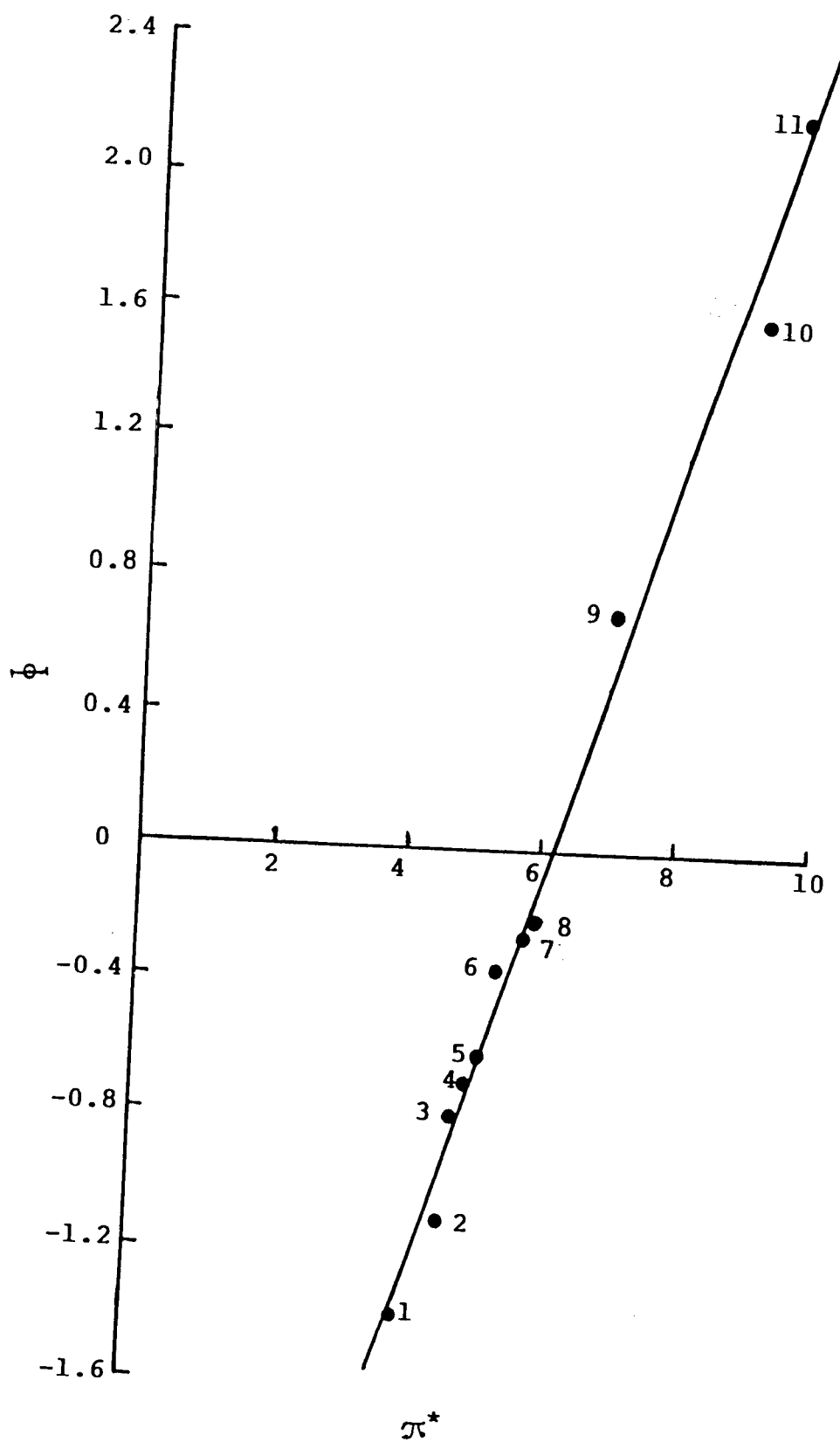


Fig. 1 Correlation between $\bar{\mu}$ and π^* for some hydrogen bond donor solvents. The solvents are numbered according to Table 1.

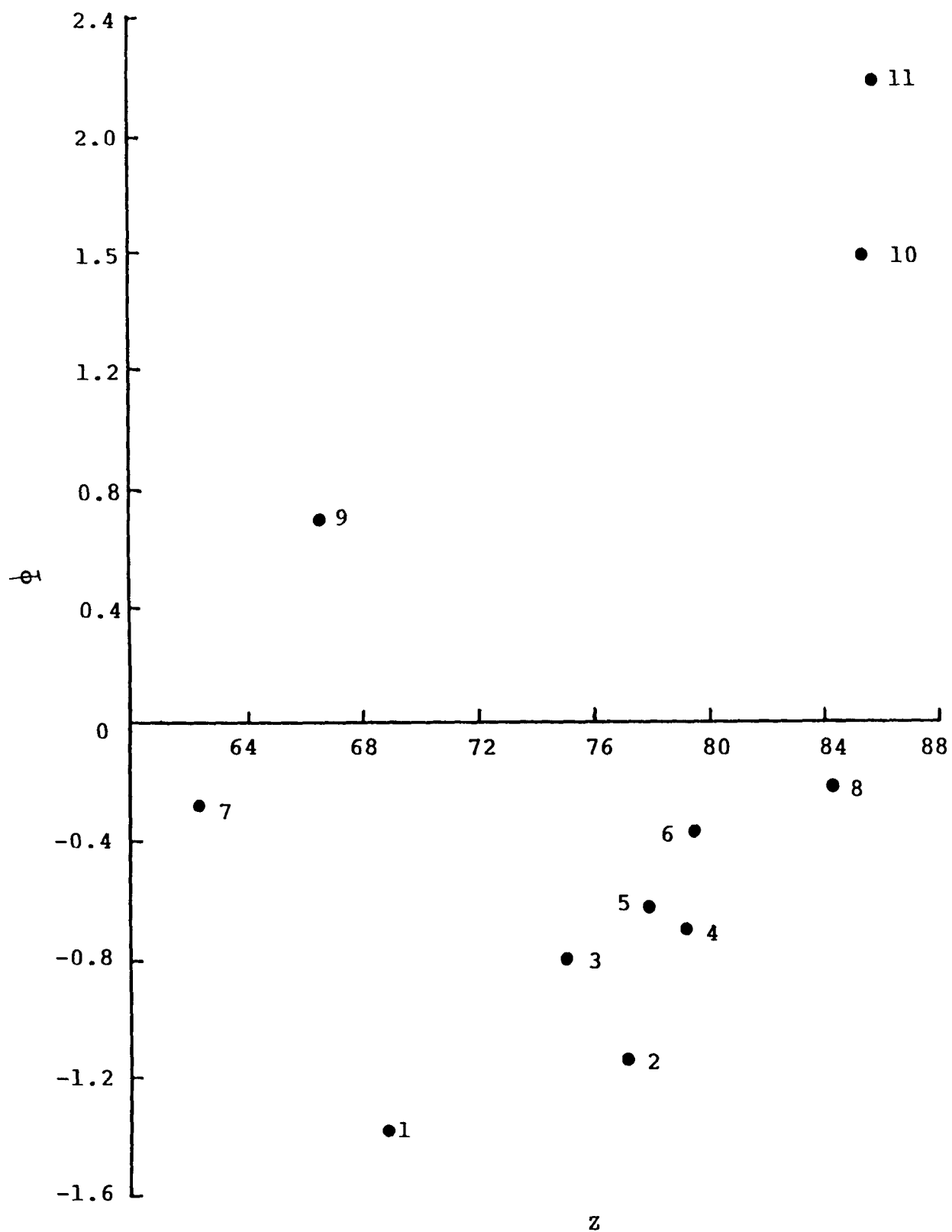


Fig. 2 Correlation between δ and Z for some hydrogen bond donor solvents. The solvents are numbered according to Table 1.

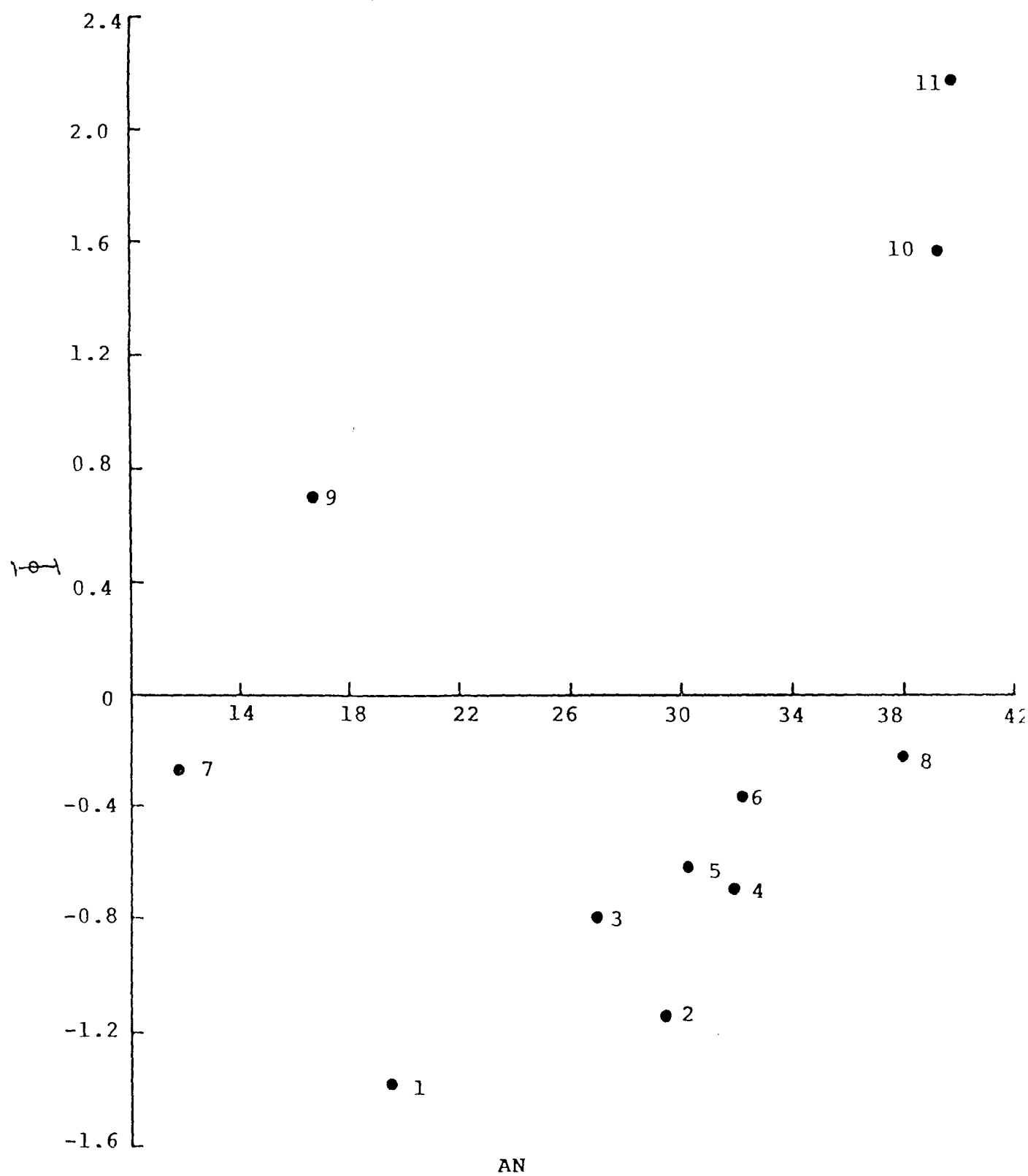


Fig. 3 Correlation between $\log K$ and AN for some hydrogen bond donor solvents. The solvents are numbered according to Table 1.

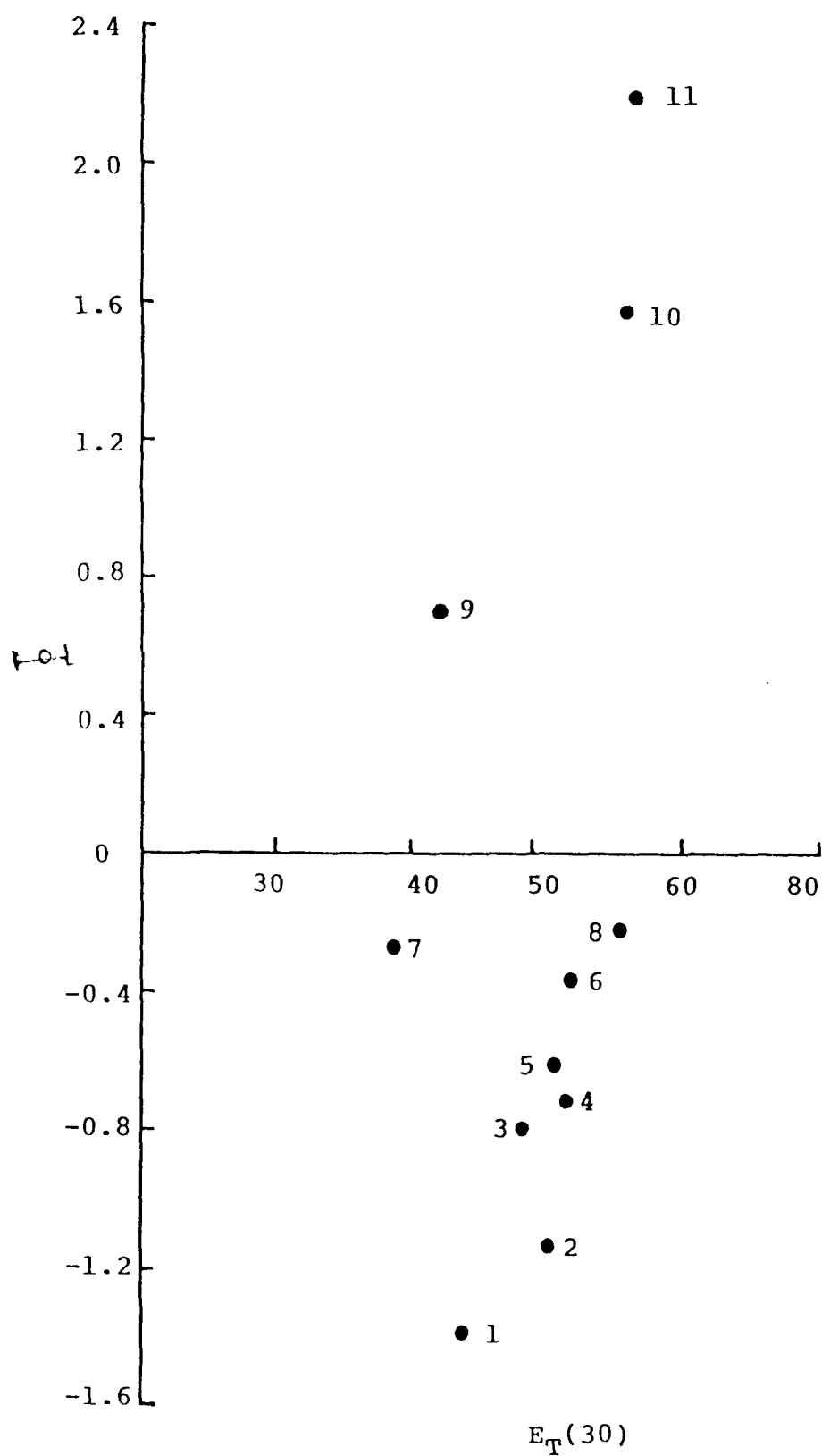


Fig. 4 Correlation between $\bar{\mu}$ and $E_T(30)$ for some hydrogen bond donor solvents. The solvents are numbered according to Table 1.

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CHAPTER - 4

CHARGE-TRANSFER Vs HYDROGEN BONDING. THE NITROMETHANE-ANILINES SYSTEMS

INTRODUCTION

Qureshi¹ had earlier proposed that the interaction of aromatic amines and dinitrobenzenes was due to charge-transfer (CT) and not hydrogen bonding. This was at variance to the studies of Thorne and Koob² whose conclusions were based solely on phase diagrams. In further studies by Qureshi et al it was finally concluded that both interactions were important³. Nitromethane (CH_3NO_2) is an interesting molecule as it is non-aromatic and contains single nitro and methyl groupings, and gives a sharp singlet in its NMR spectrum referenced to TMS as an internal standard. With increasing awareness that many hydrogen bonded systems are predominantly charge-transfer complexes⁴ it was found interesting to investigate the complexes of Nitromethane with a series of aromatic amines. Nitromethane forms yellow coloured 1:1 complexes with Aniline, N-Methylaniline, N,N-Dimethylaniline and N,N-Diethylaniline.

EXPERIMENTAL

Nitromethane was a BDH Analar reagent, Aniline and N-Methylaniline were from Riedel, N,N-Dimethylaniline and N,N-Diethylaniline were Analar reagents from BDH, Poole England. All Anilines were freshly distilled over zinc dust prior to use. The solvent used was CCl_4 (BDH, Analar). Nitromethane and CCl_4 were used as received, UV-Visible

spectral data were obtained on Elico SL 151 UV-VIS spectrophotometer and the NMR spectral data were recorded on Jeol FX-100 FT NMR spectrometer working at 100 MHz. In the UV-visible spectra Nitromethane was found to be transparent throughout the region of interest. The small absorption of Anilines was compensated by taking an equal concentration of the Anilines in the reference cell as was present in the complex. The procedure follows a method developed by Mulliken⁵. For the isolation of absorption maxima of the Nitromethane-Anilines complexes equal volumes of .1M solutions of Nitromethane and Anilines in CCl₄ were mixed and the spectra recorded against a blank containing equal concentration of Anilines as in the complex.

Equilibrium constants of Nitromethane-Anilines complexes were evaluated by optical spectroscopy using the well known Benesi-Hildebrand equation⁶ at the respective $\bar{\nu}_{\max}$ values of the complexes. A brief description of the method is as follows:

The Benesi-Hildebrand equation takes the form:

$$\frac{[A]_0}{A} = \frac{1}{K \epsilon_{\bar{\nu}}} + \frac{1}{[D]_0} + \frac{1}{\epsilon_{\bar{\nu}}}$$

where $[A]_0$ is the initial concentration of the acceptor, $[D]_0$ is the initial concentration of the donor, K is the equilibrium constant of the complex, A is the absorbance of

the complex at $\bar{\nu}$ and $\epsilon_{\bar{\nu}}$ is the molar absorptivity of the complex at $\bar{\nu}$. $[A]_0$ is kept constant and $[D]_0$ is varied and always kept in large excess over the acceptor. On plotting $[A]_0/A$ vs $1/[D]_0$ for a series of solutions under the condition $[D]_0 \gg [A]_0$, a straight line is obtained where the intercept = $1/\epsilon_{\bar{\nu}}$ and the slope = $1/K\epsilon_{\bar{\nu}}$, whereby K may be evaluated. The linearity of $[A]_0/A$ vs $1/[D]_0$ plots (Figures 1-4) is taken as an evidence for the 1:1 stoichiometry of these complexes. In the present study the equilibrium constant measurements have been carried out under the condition $[(CH_3NO_2)] \gg [Anilines]$. Though CH_3NO_2 can be an electron acceptor it has been taken in excess because even at larger concentrations it does not absorb at all in the region of $\bar{\nu}_{max}$ of these complexes. However, it does not alter the K values.

RESULTS AND DISCUSSIONS

In a study carried out previously⁷ on the interaction of β -Naphthol with $N(C_2H_5)_3$, $O(C_2H_5)_2$ and CH_3NO_2 and based on measurements of equilibrium constants employing electronic spectroscopy, variation in ionization potentials and standard values of pKa and dipole moments, the authors conclude that CH_3NO_2 is the least effective donor where charge-transfer is concerned and the overall trend favours charge-transfer over hydrogen bonding. The

results of this study are given in Table 1. In the Nitromethane - Anilines complexes the techniques that have been chiefly employed are isolation of frequencies of absorption maxima of the complexes, measurements of equilibrium constants by electronic spectroscopy and measured shifts from NMR spectrometry.

The $\bar{\nu}_{\max}$ values for various CH_3NO_2 -Anilines complexes are given in Table 2. The trend of ionization potential (I_p) of various Anilines is Aniline > N-Methylaniline > N,N-Dimethylaniline > N,N-Diethylaniline. A high ionization potential signifies a low tendency towards charge-transfer. If charge-transfer was the only mode of interaction, the sequence in $\bar{\nu}_{\max}$ values obtained would be N,N-Diethylaniline > N,N-Dimethylaniline > N-Methylaniline > Aniline. However, the reverse trend obtained here, though favouring hydrogen bonding does not rule out charge-transfer because N,N-Dimethylaniline and N,N-Diethylaniline show new absorption maxima at 26809 cm^{-1} and 26525 cm^{-1} respectively, even though they cannot form hydrogen bonded complexes as the protons are attached to carbon and not nitrogen; any hydrogen bonding, even if it did occur, would be too weak to be detectable by techniques used. The fact that N,N-Dimethylaniline and N,N-Diethylaniline complexes show new absorption maxima even in the absence of hydrogen bonding ability signifies that both hydrogen bonding and

TABLE - I
VARIOUS PARAMETERS FOR β -NAPHTHOL COMPLEXES (DATA FROM REFERENCE 7)

Proton Donor	Proton Acceptor	Equilibrium constant K (LM^{-1})	$\Delta\bar{\nu}_{\text{max}}$ (cm^{-1})	I_p	pKa	Dipole Moment
β -Naphthol (n-heptane)	$\text{N}(\text{C}_2\text{H}_5)_3$	103(25°C)	590	7.5	10.72	0.82
	$\text{O}(\text{C}_2\text{H}_5)_2$	14.5(25°C)	410	9.53	-3.0	1.13
	CH_3NO_2	2.6(25°C)	190	10.33	-11.38	350

Note: A point to be noted here is that K values are far too high and contributions of electrostatic forces cannot be ruled out.

TABLE - 2

 $\bar{\nu}_{\max}$ VALUES FOR CH_3NO_2 -ANILINES COMPLEXES

Complex	$\bar{\nu}_{\max}$ (cm^{-1})
CH_3NO_2 - Aniline	27397
CH_3NO_2 - N-Methylaniline	27473
CH_3NO_2 - N,N-Dimethylaniline	26809
CH_3NO_2 - N,N-Diethylaniline	26525

charge-transfer contribute to the stability of the complexes between CH_3NO_2 and Anilines.

It is also seen (Table 2) that N-Methylaniline complex shows a reversal in the trend. Such an erratic trend has been obtained earlier between dinitrobenzenes and Anilines³. It was explained that N-Methylaniline has only one NH proton for hydrogen bonding (compared to two for Aniline) and at the same time possesses a lower ionization potential, making it a better contestant for charge-transfer. Therefore, N-Methylaniline has a lower probability (than Aniline) to form a hydrogen bonded complex and a higher probability to form a charge-transfer complex; the net result seems to be some compromise between the two. It was also emphasised³ that an erratic trend may sometimes appear if the complexes are strongly hydrogen bonded and simultaneously show a strong charge-transfer.

The equilibrium constants of the CH_3NO_2 -Anilines complexes are listed in Table 3. A glance at Table 3 shows that the trend in the values of K reinforces the conclusions reached by the trend of $\bar{\nu}_{\text{max}}$ values except with the difference that now N-Methylaniline no longer deviates from the trend. However, it would be rather difficult to agree that such a discrepancy does not exist here. Firstly, the differences in K obtained for Aniline and N-Methylaniline complexes are rather small. Furthermore,

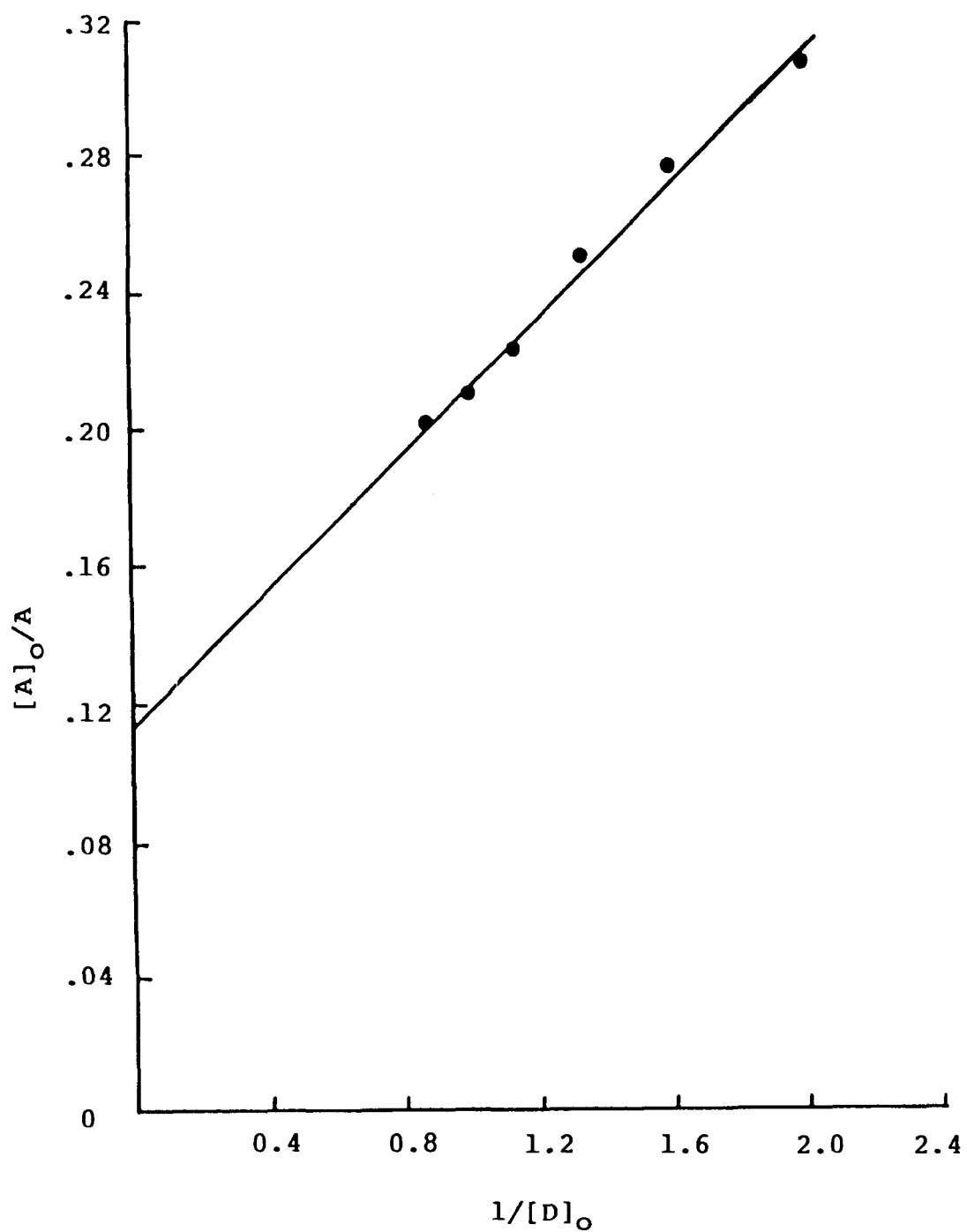


Fig. 1 The Benesi-Hildebrand plot for the evaluation of the equilibrium constant of the Nitromethane-Aniline complex at 27397 cm^{-1} .

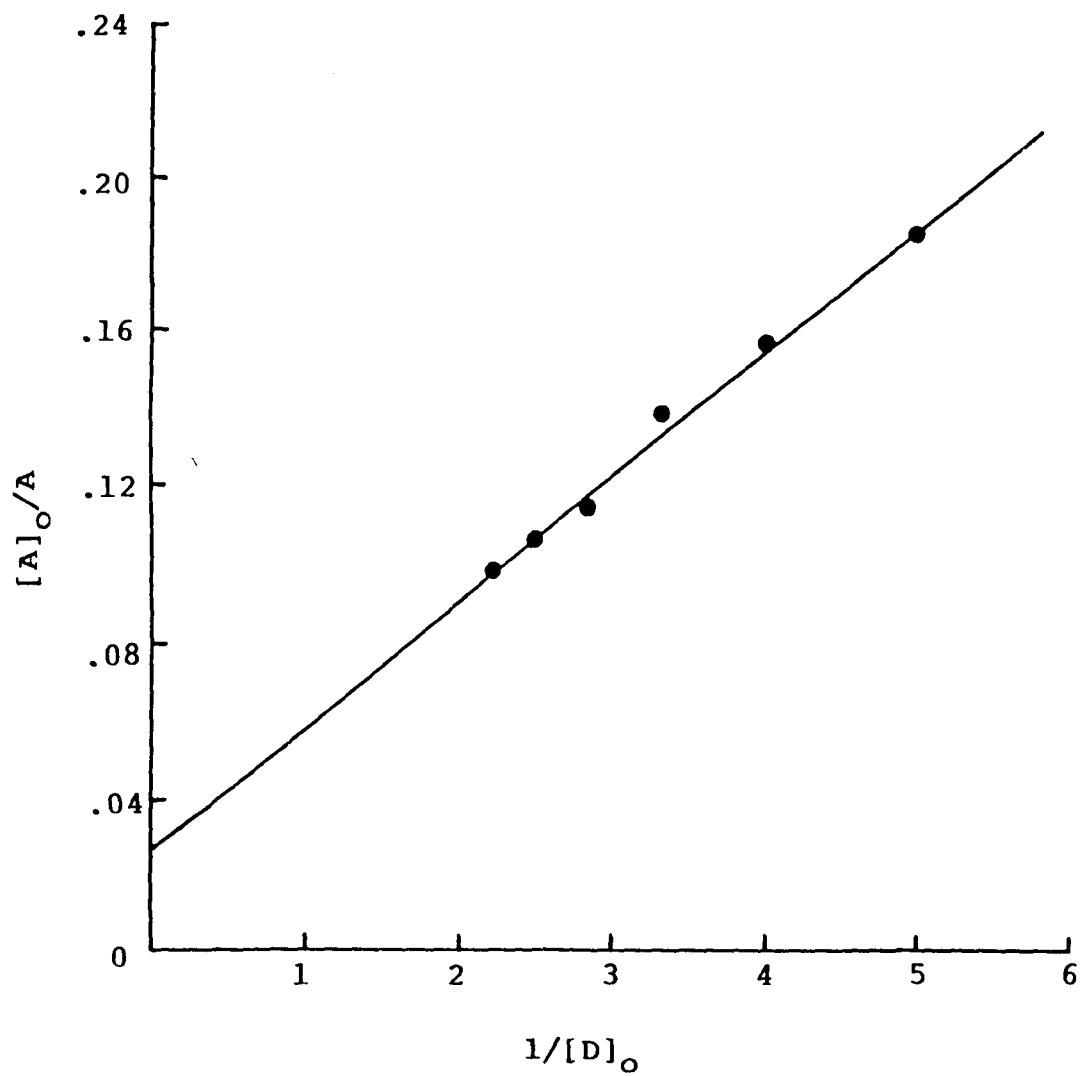


Fig. 2 The Benesi-Hildebrand plot for the evaluation of the equilibrium constant of the Nitromethane-N-Methylaniline complex at 27473 cm^{-1} .

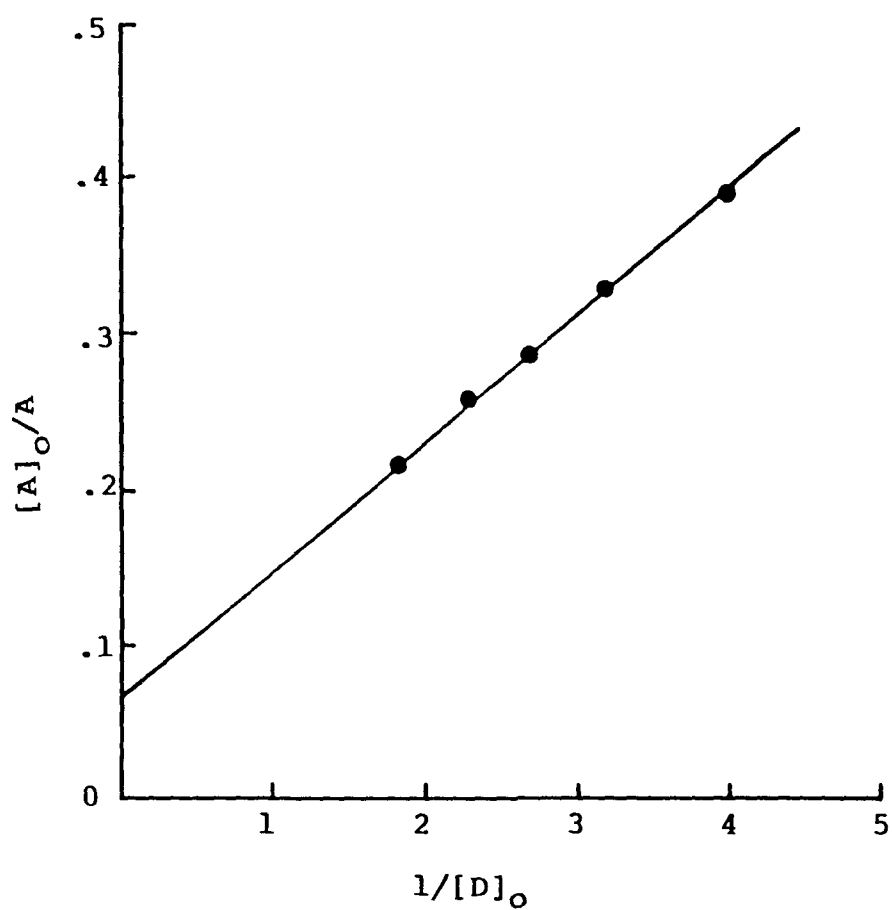


Fig. 3 The Benesi-Hildebrand plot for the evaluation of the equilibrium constant of the Nitromethane-N,N-Dimethylaniline complex at 26809 cm^{-1} .

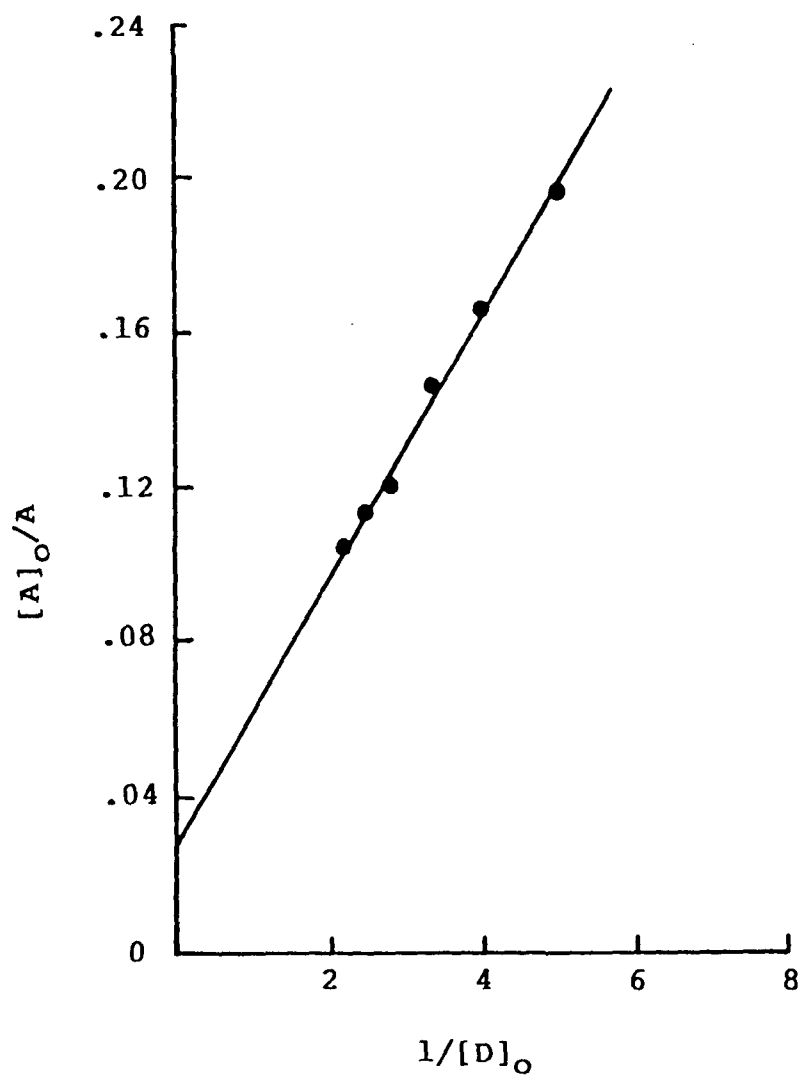


Fig. 4 The Benesi-Hildebrand plot for the evaluation of the equilibrium constant of the Nitromethane-N,N-Diethylaniline complex at 26525 cm^{-1} .

TABLE - 3

EQUILIBRIUM CONSTANTS FOR CH_3NO_2 -ANILINES COMPLEXES

Complex	K (Litre Mol ⁻¹)
CH_3NO_2 - Aniline	0.99 (25°C)
CH_3NO_2 - N-Methylaniline	0.95 (25°C)
CH_3NO_2 - N,N-Dimethylaniline	0.70 (25°C)
CH_3NO_2 - N,N-Diethylaniline	0.31 (25°C)

in spectrophotometric measurements (especially in evaluation of K) often there are contributions from electrostatic interactions⁸, and though it is possible to evaluate accurately K , their separation to obtain K is rather problematic⁹. However, the interesting feature is that the trend of measured K values again predicts the simultaneous contributions from hydrogen bonding and charge-transfer to the complexes of CH_3NO_2 and Anilines.

In ^1H NMR spectral shift measurements, the CH_3NO_2 resonance appears as a sharp singlet ($\delta = 4.35$) (Figure 5). The NH protons of Aniline and N-Methylaniline also appear as sharp singlets ($\delta = 3.37$ and $\delta = 3.44$ respectively) (Figure 6). The aromatic protons of the anilines give very complex patterns and are difficult to decipher. On complexation the CH_3NO_2 singlet moves to lower frequencies while the NH protons of Anilines move to higher frequencies (Figures 7 and 9). However, the shift of NH protons to higher frequencies is not very diagnostic because the electron density around the NH protons would decrease in both charge-transfer as well as hydrogen bonding. A shift of CH_3NO_2 singlet to lower frequencies again would be expected both in the case of charge-transfer and hydrogen bonding. The alkyl protons of N,N-Diethylaniline and N,N-Dimethylaniline (Figures 8 and 9) move to higher

frequencies. This, however, is an indication of charge-transfer alone. To confirm the contribution of hydrogen bonding to the complexes of Nitromethane and Anilines Δ_o values, which are theoretical values that predict the shifts at complete complexation, were evaluated. The measured NMR shifts of CH_3NO_2 singlet were converted to Δ_o by Hanna-Ashbaugh equation¹⁰. Δ_o values were computed with respect to the resonance of free CH_3NO_2 . These are listed in Table 4. Δ_o values show the following sequence: Aniline > N-Methylaniline > N,N-Dimethylaniline > N,N-Diethylaniline. This is probably because Aniline is capable of forming both hydrogen bonded and charge-transfer complexes and the high value of Δ_o probably predicts that both processes reinforce each other.

The trend of data in Tables 2, 3 and 4 clearly indicates that hydrogen-bonding contributes to the complexes between Nitromethane and Anilines, in as much as Aniline with minimum tendency towards charge-transfer (due to highest I_p) and maximum probability for hydrogen bonding (having two NH protons) forms the strongest complex (in the present series) with Nitromethane, followed by N-Methylaniline (with only one NH proton). N,N-Dimethylaniline and N,N-Diethylaniline with zero probability for hydrogen bonding form less stable complexes with nitromethane due to charge-transfer alone. The higher stability of the

N,N-Dimethylaniline complex than N,N-Diethylaniline complex (against the I_p values) is probably due to the steric effect as the ethyl groups are more bulky as compared to methyl groups.

In conclusion it can now safely be said that CH_3NO_2 forms both charge-transfer and hydrogen bonded complexes with aromatic amines.

TABLE - 4

 ^1H NMR Δ_{O} VALUES FOR CH_3NO_2 -ANILINES COMPLEXES

Complex	Δ_{O} (Hz)
CH_3NO_2 - Aniline	173.39
CH_3NO_2 - N-Methylaniline	107.41
CH_3NO_2 - N,N-Dimethylaniline	66.48
CH_3NO_2 - N,N-Diethylaniline	55.88

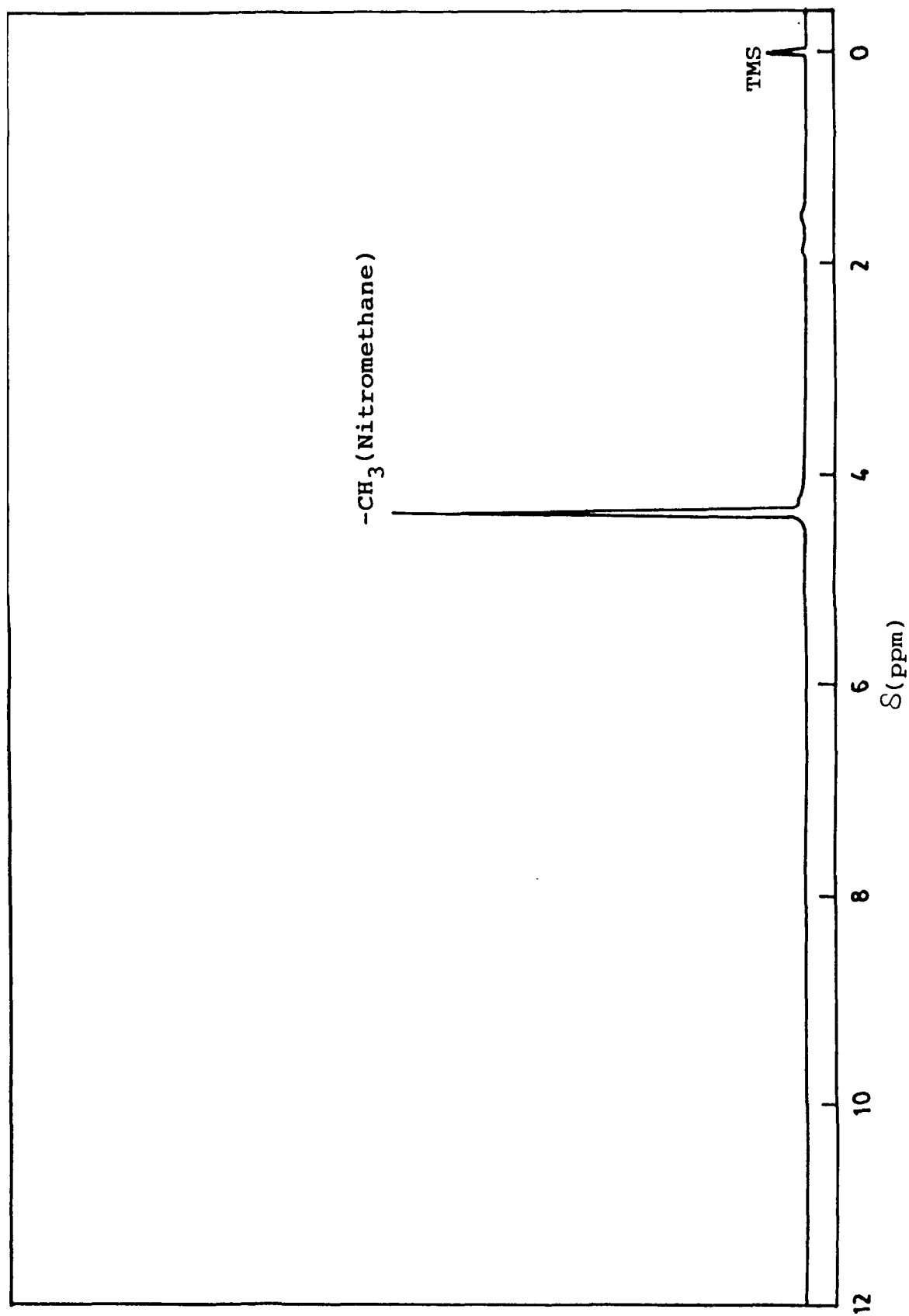


Fig. 5 ^1H NMR spectrum of Nitromethane in CCl_4

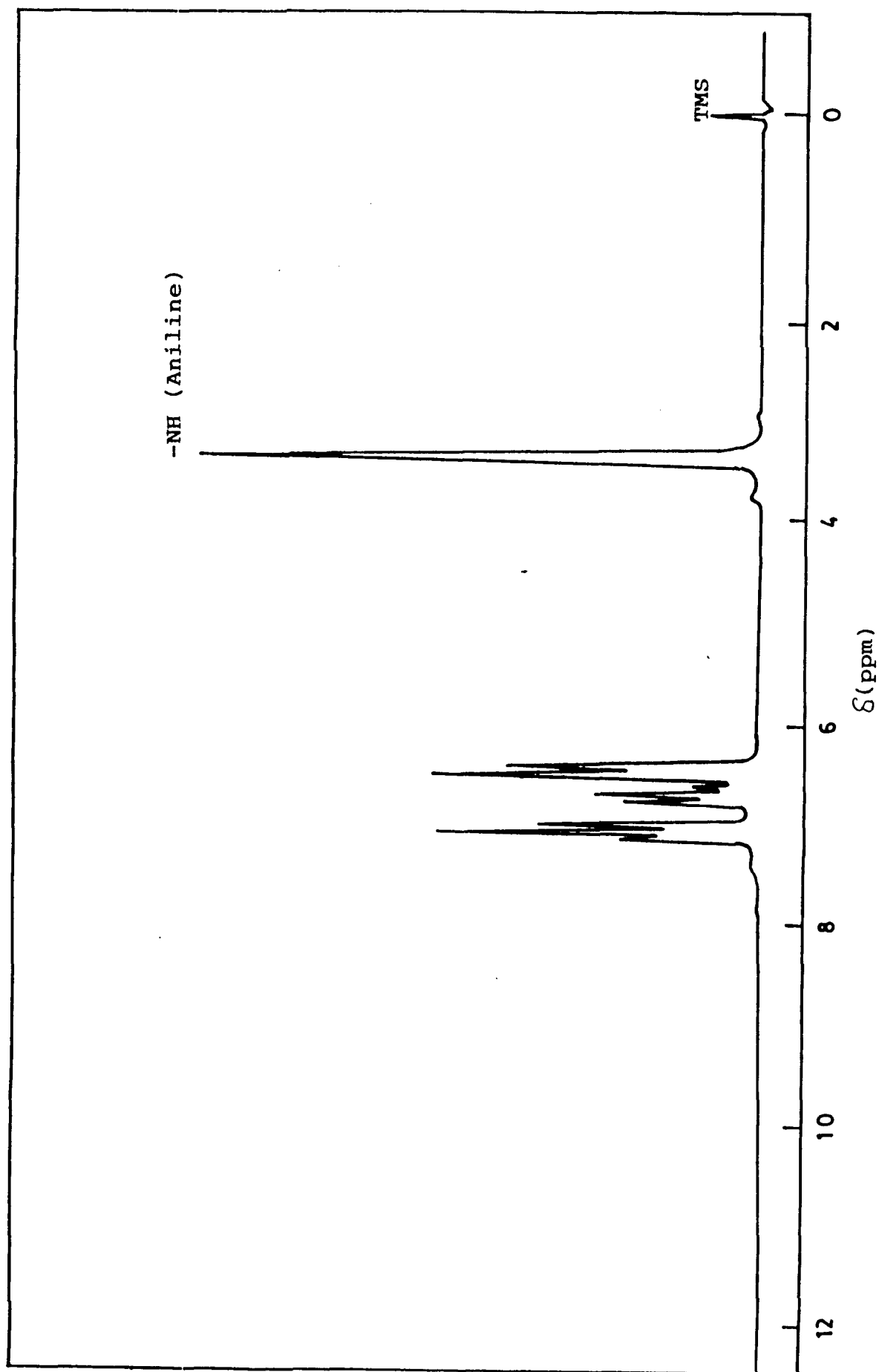


Fig. 6 ^1H NMR spectrum of Aniline in CCl_4 .

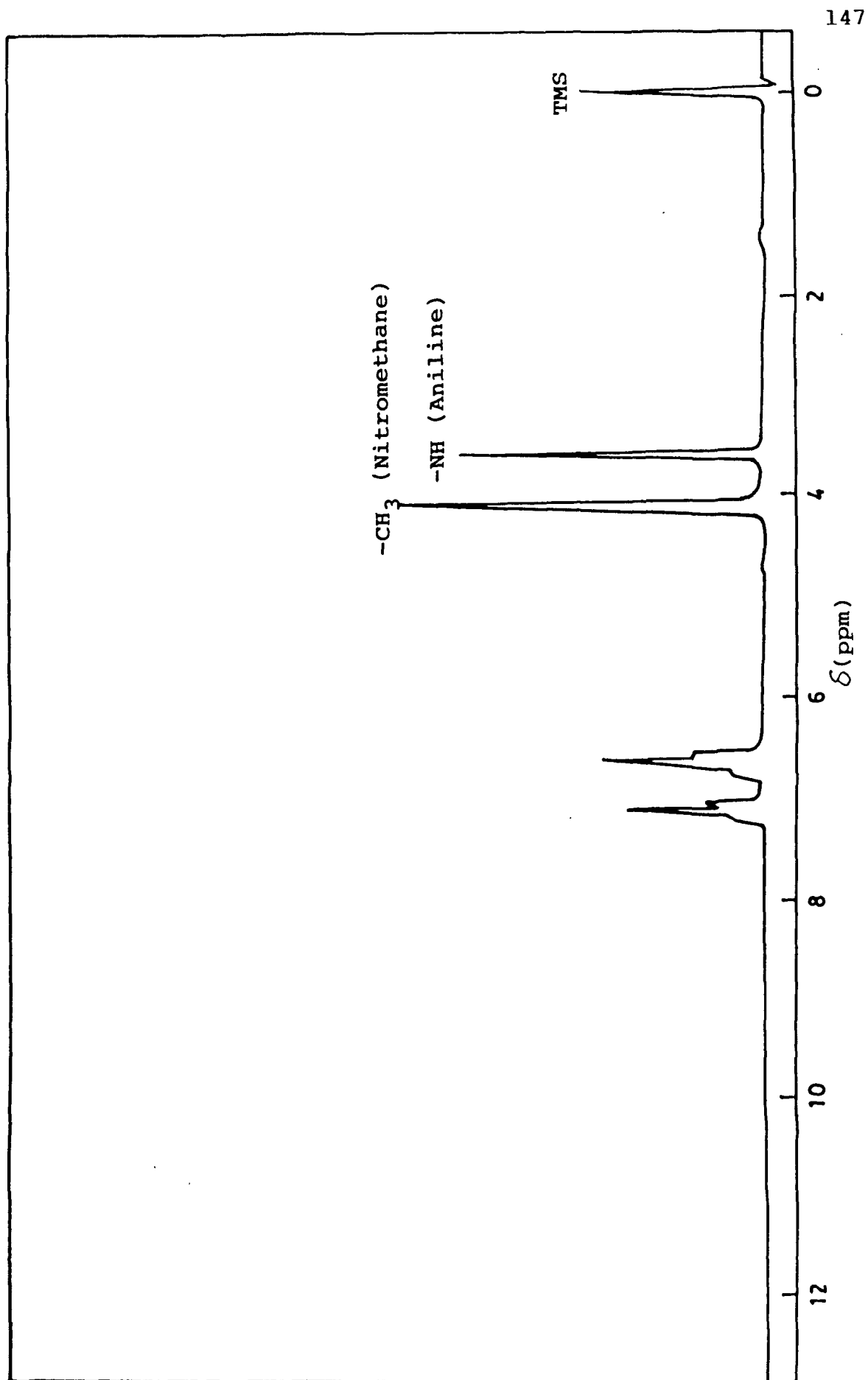


Fig. 7 ^1H NMR spectrum of the Nitromethane-Aniline complex in CCl_4 .

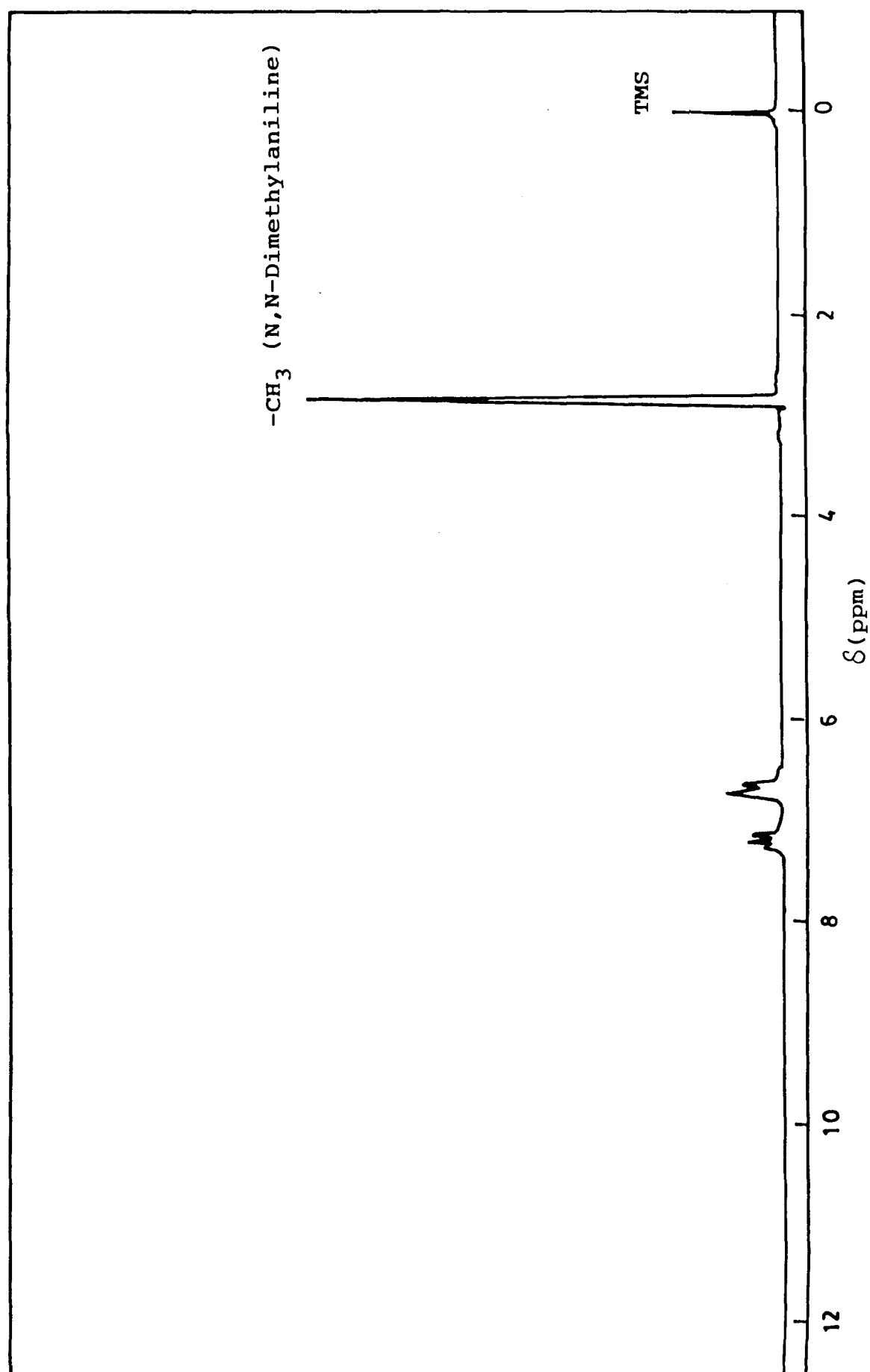


Fig. 8 ^1H NMR spectrum of N,N-Dimethylaniline in CCl_4 .

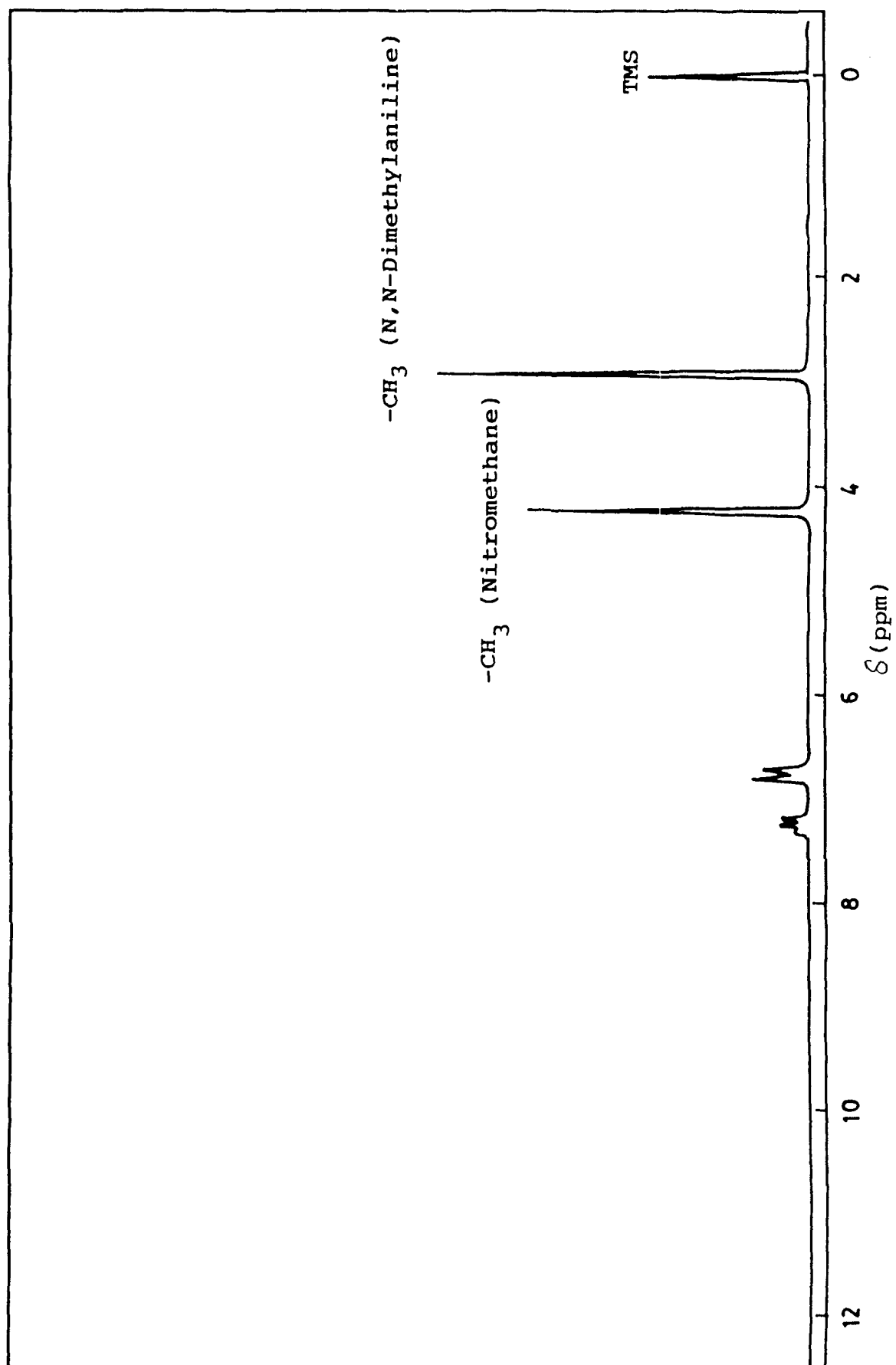


Fig. 9 ^1H NMR spectrum of the Nitromethane - N,N-Dimethylaniline complex in CCl_4 .

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CHAPTER - 5

MULTIPLE CHARGE-TRANSFER BANDS IN THE REACTION
OF TRIPHENYLANTIMONY WITH 1-CHLORO-2,4-
DINITROBENZENE

INTRODUCTION

Charge-transfer complexes of organometallic donors have been studied extensively. Some of these studies¹⁻⁵ reflect the importance of these complexes. Though complexes with alkyl donors have been studied extensively their phenyl counterparts have been much less studied. In the present study it is shown that 1-chloro-2,4-dinitrobenzene forms a molecular complex with triphenylantimony in both solid and solution. This complex shows a multiple charge-transfer spectrum centered at 380 and 394.5 nm. IR studies have been carried out and equilibrium constant has been measured. Preliminary solid state studies by Rastogi's capillary technique⁶ has also been carried out.

EXPERIMENTAL

Triphenylantimony was A.R. Grade from Fluka and 1-chloro-2,4-dinitrobenzene was G.R. Grade from E. Merck, Darmsadt Germany. Both triphenylantimony and 1-chloro-2,4-dinitrobenzene were used as received. CCl_4 (Analar, BDH Pool England) was used as solvent in the solution studies. UV-Visible studies were carried out on Elico SL 151 UV-VIS Spectrophotometer. FT-IR spectra were recorded on Nicolet 5DX FT-IR Spectrophotometer. FT-NMR spectra were recorded on Jeol FX 100 FTNMR Spectrometer working at 99.55 MHz using TMS as internal reference.

RESULTS AND DISCUSSION

A UV-visible spectrum of 1-chloro-2,4-dinitrobenzene (CDB) in CCl_4 shows a broad featureless band centered at 320 nm while that of triphenylantimony (TPA) shows an absorption maximum at 298 nm. 1-chloro-2,4-dinitrobenzene and triphenylantimony form a yellow coloured charge-transfer complex in CCl_4 . The complex of CDB and TPA was prepared by mixing equal volumes of .016M CDB and .027M TPA solutions in CCl_4 . The UV-visible spectrum was recorded after taking an equal concentration of CDB in the reference cell. This was done to compensate for the small absorption of CDB in the region of charge-transfer bands. This procedure follows a method developed by Mulliken⁷. Two bands appeared in the spectrum of the complex. These are centered at 380 and 394.5 nm. Therefore CDB-TPA complex is a case of multiple charge-transfer complex. The band multiplicity may arise from electron donation from more than one energy level in the donor to more than one energy level in the acceptor⁸. According to McGlynn two isomeric complexes are formed if the maximum overlap principle is applied⁹. Figure 1 shows the two charge-transfer bands of the CDB-TPA complex.

FT-IR studies were carried out in solution and by KBr disk method as well. In KBr disk method equimolar quantities of finely powdered CDB and TPA were mixed and

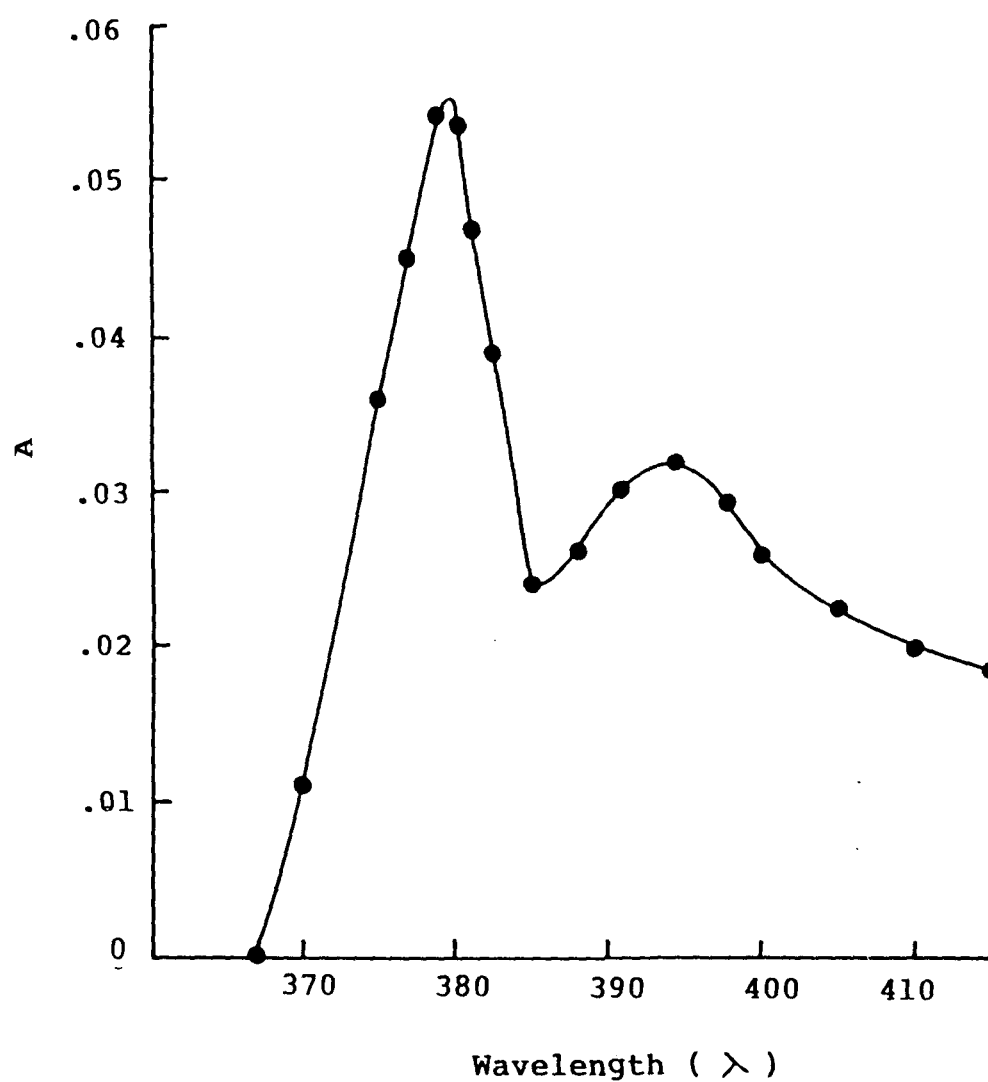


Fig. 1 The multiple charge-transfer bands of the Triphenylantimony-1-chloro-2,4-dinitrobenzene complex.

the reaction initiated in an oven controlled at a temperature of 309K, a yellow coloured complex resulted which was then mixed with KBr.

After a systematic study of 40 molecular complexes with picric acid Kross¹⁰ has postulated certain regularities in the IR spectra of acceptor molecule. According to Kross only the NO₂ asymmetric stretching vibrations showed significant changes. Assuming that the NO₂ group of CDB behaves similar to the NO₂ group of picric acid, it is possible to interpret the IR spectrum of the CDB-TPA complex on the basis of the studies of Kross. CDB shows a broad band centered at 1530 cm⁻¹ and another at 1600 cm⁻¹ due to nitro asymmetric stretching vibrations. In the complex, while the 1600 cm⁻¹ band remains without shift, the broad band localized at 1530 cm⁻¹ shifts to 1535 cm⁻¹. A shift of 5 cm⁻¹ shows a weak interaction. As per Kross classification these features indicate that in addition to $\pi-\pi^*$ bonding there is a localized intermolecular interaction. The weak $\pi-\pi^*$ interaction could be due to the π orbitals of CDB and π orbitals of the benzene ring of TPA. The localized intermolecular interaction is probably due to the contribution of the metal to the complex.

After surveying the IR spectra of several related organometallic compounds, one comes to the conclusion that the metal-C bands lie somewhere close to 1400 cm⁻¹. I

therefore, ascribe the band at 1430 cm^{-1} in free TPA to Sb attached to a phenyl ring. A band in this position is not present in the spectrum of CDB. In the complex this peak shifts to 1435 cm^{-1} ; again showing a shift of 5 cm^{-1} (towards lower frequency) as in the case of nitro asymmetric stretching band. As mentioned a shift of 5 cm^{-1} shows a weak charge-transfer complexation. In solution again the nitro asymmetric absorption shows a shift of 5 cm^{-1} to lower frequencies.

In the FT-NMR spectrum in CCl_4 the resonances of the three protons of CDB are located at $\delta 8.1$, $\delta 8.7$ and $\delta 9.05$ and do not show any shifts in the complex probably due to the fact that it is a weak charge-transfer complex and the electron density gained by the acceptor (CDB) is distributed throughout the molecule. The single peak of TPA ($\delta = 7.4$) however, shows a shift of 4 Hz signifying again a weak interaction. The low solubility of TPA precluded further investigation.

To study the nature of the yellow coloured complex in the solid state, a simple procedure was devised. 30 mg of solid CDB (finely powdered) was placed in two small glass bulbs. To one bulb was added 30 mg of finely powdered TPA and the reaction initiated at 309 K until a yellow coloured complex was formed. Equal amount of solvent was added to both the bulbs to dissolve the constituents.

The UV-visible spectrum was recorded again with CDB solution in the reference cell. The spectrum obtained showed the same two maxima centered at 380 and 394.5 nm as in the solution spectrum. This shows that the products of the reaction in the solid state and solution are the same.

The solid state reaction between CDB and TPA was carried out by placing well powdered samples with uniform particle sizes in a glass capillary from either end till they met at a junction. The capillary was placed in an oven controlled at a temperature of 309 K. Yellow colour developed at the boundary of CDB and TPA and moved towards CDB showing that TPA diffuses into CDB in the solid state reaction. The movement of the coloured boundary in CDB was recorded as a function of time. The kinetic plot is given in figure 2. The rate equation followed is:

$$\xi = 4.125 \log t - 1.6$$

Association constant K was evaluated by the method of Foster¹¹ under the condition $[A]_0 = [D]_0$ and applying the equation

$$\frac{[A]_0}{A} = \frac{1}{K \epsilon_{\lambda}} \cdot \frac{1}{[D]_0} + \frac{2}{\epsilon_{\lambda}}$$

where $[A]_0$ is the initial concentration of acceptor equal to $[D]_0$, the initial concentration of the donor, A is the absorbance of the complex at λ , K is the association

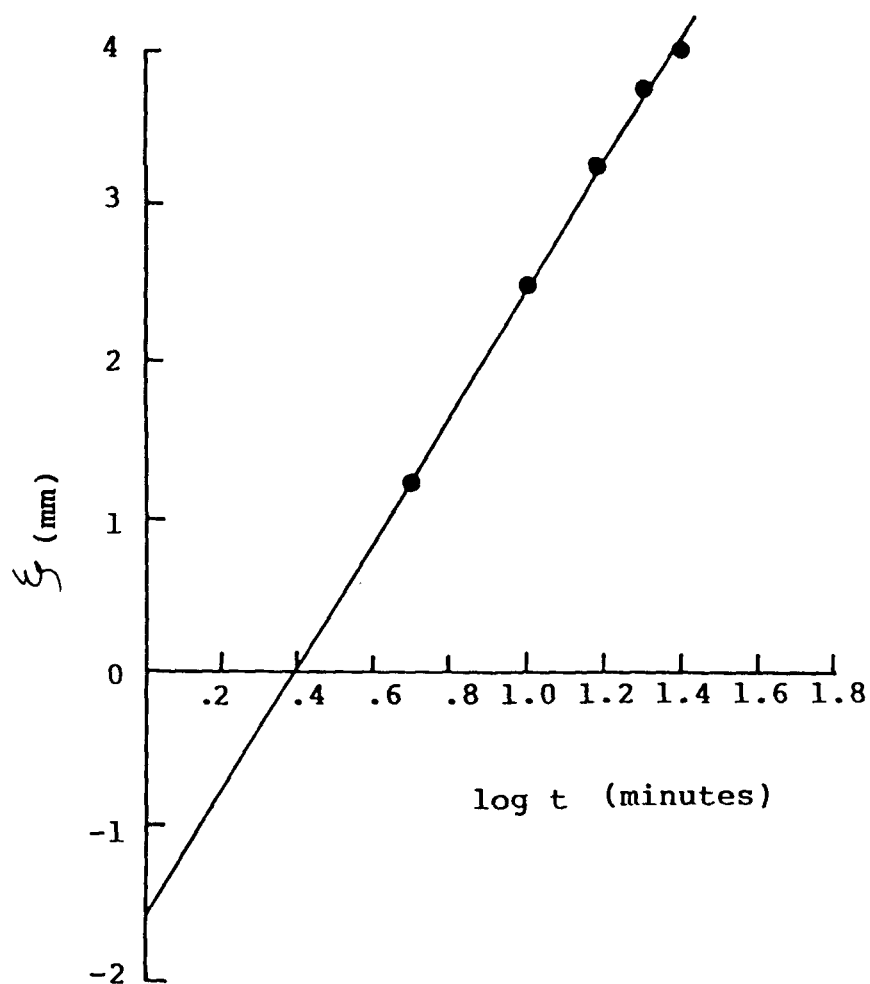


Fig. 2 The kinetic plot of solid state reaction between Triphenylantimony and 1-Chloro-2,4-dinitrobenzene (by the capillary method of Rastogi and Dubey⁶)

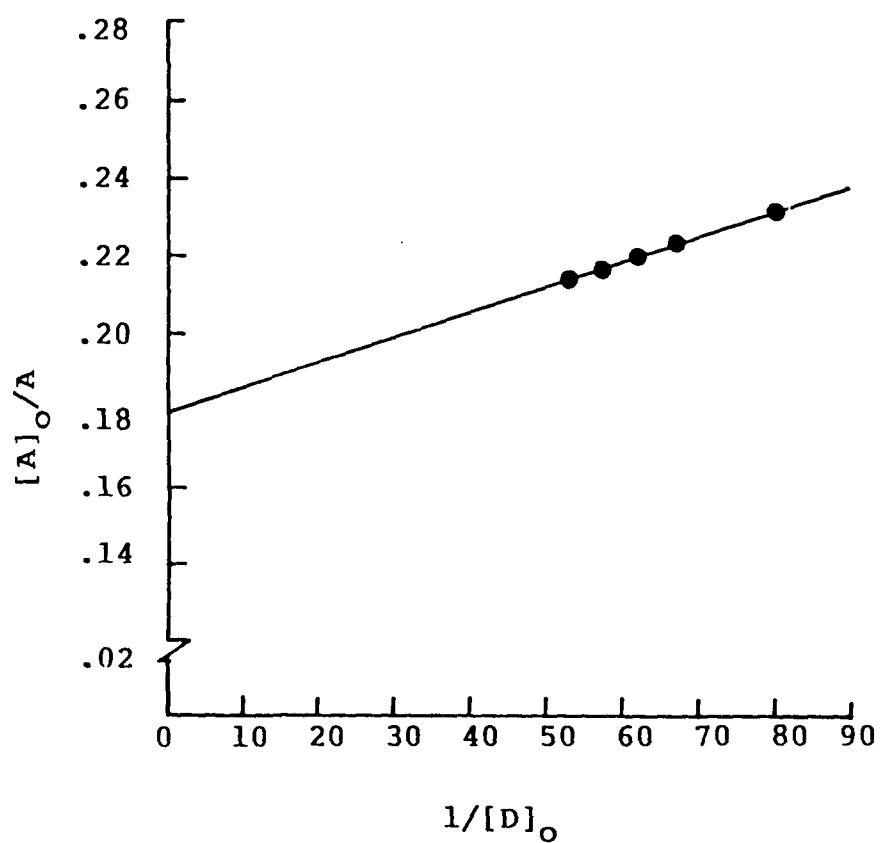


Fig. 3 The Foster's plot for the evaluation of the association constant of the Triphenyl-antimony-1-Chloro-2,4-dinitrobenzene complex at 400 nm.

constant and ϵ_{λ} is the molar absorptivity of the complex at λ . On plotting $[A]_0/A$ vs $1/[D]_0$ for a series of solutions a straight line is obtained under the condition $[A]_0 = [D]_0$ with the slope equal to $1/K\epsilon_{\lambda}$ and the intercept equal to $2/\epsilon_{\lambda}$ (Figure 3). This study was carried out at 400 nm with the concentrations ranging from .0125 to .02 M. The value of K came out to be 13.88 LMol^{-1} and the value of ϵ_{400} 11.11.

In conclusion one can say that CDB and TPA form a yellow coloured weak charge-transfer complex in CCl_4 as well as in solid state. It is a case of multiple charge-transfer complex; the two charge-transfer bands being centered at 380 and 394.5 nm. UV-VIS spectral studies also show that the products of the reaction between CDB and TPA in the solid state and the solution are the same. The IR studies suggest that there is an interaction between Sb of TPA and CDB besides the $\pi-\pi^*$ interaction between the π orbitals of CDB and π orbitals of the benzene rings of TPA.

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CHAPTER - 6

AN NEW SIMPLE EQUATION FOR MOLECULAR COMPLEXES.

AN IMPROVEMENT OVER THE BENESI-HILDEBRAND
EQUATION. FIRST EVIDENCE FOR NMR ASSOCIATION
CONSTANTS BEING INDEPENDENT OF
THE METHODS USED

INTRODUCTION

The Benesi-Hildebrand method¹, for the evaluation of association constants for molecular complexes by electronic spectroscopy was the first and perhaps the most popular method. Later several modifications of the Benesi-Hildebrand equation appeared in the literature, each claiming some superiority or other. The Benesi-Hildebrand equation takes the form:

$$\frac{[A]_0}{A} = \frac{1}{K \epsilon_\lambda} \frac{1}{[D]_0} + \frac{1}{\epsilon_\lambda} \quad \dots (1)$$

Where $[A]_0$ is the initial concentration of the acceptor and is kept constant throughout, $[D]_0$ is the initial concentration of the donor and is varied and always kept in large excess over the acceptor, K is the association constant, and ϵ_λ is the molar absorptivity and A is the absorbance of the complex at wavelength λ . A plot of $[A]_0/A$ vs $1/[D]_0$ is linear with the intercept equal to $1/\epsilon_\lambda$ and the slope equal to $1/K\epsilon_\lambda$. The estimation of K by this method leads to the separation of $K\epsilon_\lambda$. Though $K\epsilon_\lambda$ can be evaluated accurately, K alone cannot².

Two of such methods which proved useful are the ones by Foster³ and Scott⁴. Foster's method is based on the equation:

$$\frac{A}{[D]_0} = -KA + K[A]_0\epsilon_\lambda \quad \dots (2)$$

A plot of $A/[D]_0$ vs A should be linear with the negative slope giving K directly. The restrictive condition $[D]_0 \gg [A]_0$ is assumed. However, the equation by Foster seems to be applicable only when the concentration of the donor is far too large as compared to the acceptor. This is a rather severe restriction as on many occasions this does not obtain due to a variety of reasons e.g. solubility reasons. An inherent advantage of Foster's method is that K can be obtained directly, without recourse to any separation of terms. At the same time it is usually not easy to obtain ϵ_λ by this method.

The Scott equation is also a basis for a method to evaluate K and ϵ_λ and takes the form:

$$\frac{[D]_0 [A]_0}{A} = \frac{[D]_0}{\epsilon_\lambda} + \frac{1}{K \epsilon_\lambda} \quad \dots (3)$$

A plot of $[D]_0 \cdot [A]_0/A$ vs $[D]_0$ should be linear if $[D]_0 \gg [A]_0$. Here the slope = $1/\epsilon_\lambda$ and the intercept = $1/K\epsilon_\lambda$. The method of Scott also requires too high a difference between donor and acceptor concentrations and here too separation of terms is required to estimate K .

More recently Pushkin-Varshney-Kamoonpuri⁵ equation was proposed to determine the association constants of sparingly soluble compounds. It takes the form:

$$\frac{1}{A} = \frac{1}{K \epsilon_\lambda [A]_0} - \frac{1}{[D]_0} + \frac{1}{[A]_0 \epsilon_\lambda} \quad \dots (4)$$

A plot of $1/A$ vs $1/[D]_0$ gives a straight line with the intercept equal to $1/[A]_0 \epsilon_\lambda$ and the slope equal to $1/K \epsilon_\lambda [A]_0$. By dividing intercept by slope we can get K . The method does not require the acceptor concentration $[A]_0$ to be known. Here too the separation of terms is required to evaluate K .

A problem that has existed right from the beginning is the separation of terms (usually $K \epsilon_\lambda$). Though this drawback of the original Benesi-Hildebrand method has been partially overcome by Foster, there is need of a method that conserves the simplicity of the Benesi-Hildebrand method and yet can evaluate K independently (without recourse to any separation) and ϵ_λ reliably.

I now propose a new equation which is not only successful for these objectives but also gives acceptable results even in those situations where Foster and Scott methods fail.

EXPERIMENTAL

The reagents used were either GR or AR grade reagents from E. Merck, BDH or Fluka. The nitro compounds were recrystallised till their melting points agreed with reported values. Aniline was distilled thrice over zinc dust and stored in a dark bottle. The solvents used were CCl_4 (BDH Analar) and ethanol (absolute). All results were

obtained on SYSTRONICS-105 spectrophotometer. All measurements were carried out at 303 K under the condition $[D]_0 \gg [A]_0$, keeping $[A]_0$ constant and varying $[D]_0$.

RESULTS AND DISCUSSIONS

The molecular complexes of some dinitrobenzenes have been studied with aniline and were characterised as well defined charge-transfer complexes^{6,7}. In the present study other dinitrobenzenes have been studied as well.

As mentioned earlier the Benesi-Hildebrand equation requires the separation of terms $(K\epsilon_\lambda)$ to obtain K . This problem has been reviewed extensively². Since for the compounds in question, all K 's are rather small and ϵ_λ 's much larger, the error in K may be formidable.

I now propose a new equation which takes the form:

$$\frac{1}{[D]_0} = \frac{[A]_0}{A} \cdot K\epsilon_\lambda - K \quad \dots (5)$$

A plot of $1/[D]_0$ vs $[A]_0/A$ is linear. The negative intercept gives K directly and ϵ_λ may be obtained from the slope. It is true that for ϵ_λ a separation of terms is required. However, now the situation is not as difficult as in the case of the Benesi-Hildebrand equation. For one, K is usually very small and hence changes in K will introduce small errors in ϵ_λ . Moreover, since ϵ_λ is very large the

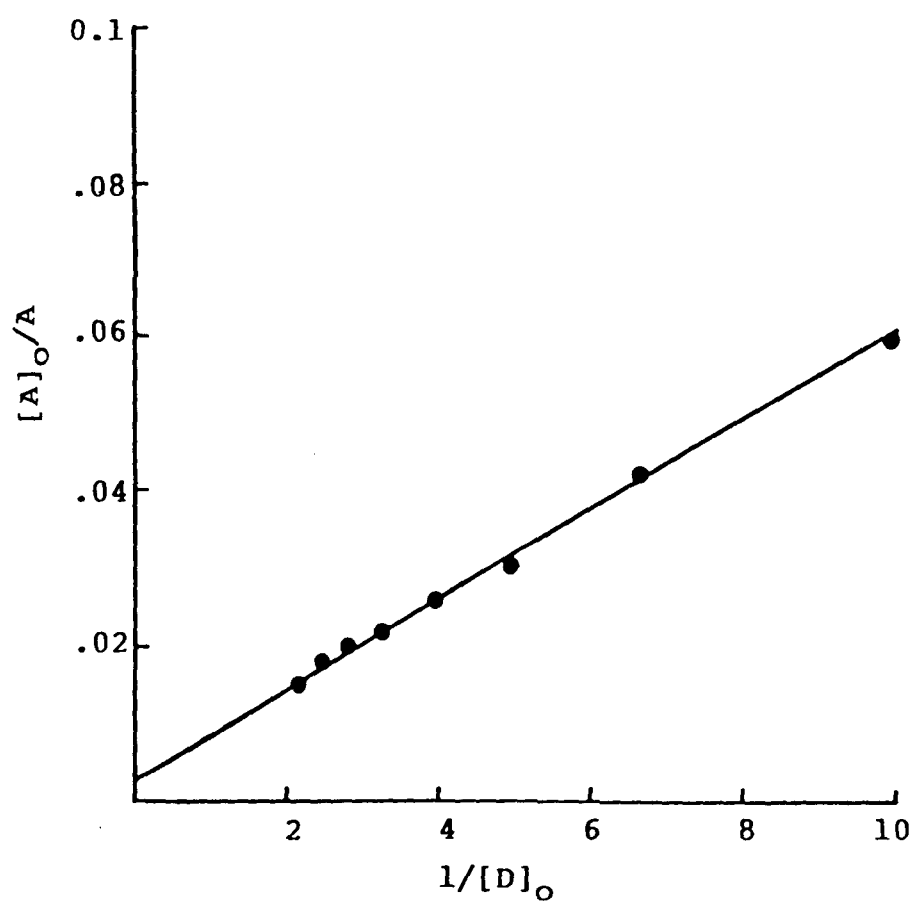


Fig. 1 The Benesi-Hildebrand plot for the 3,5-Dinitrobenzoic acid-Aniline system.

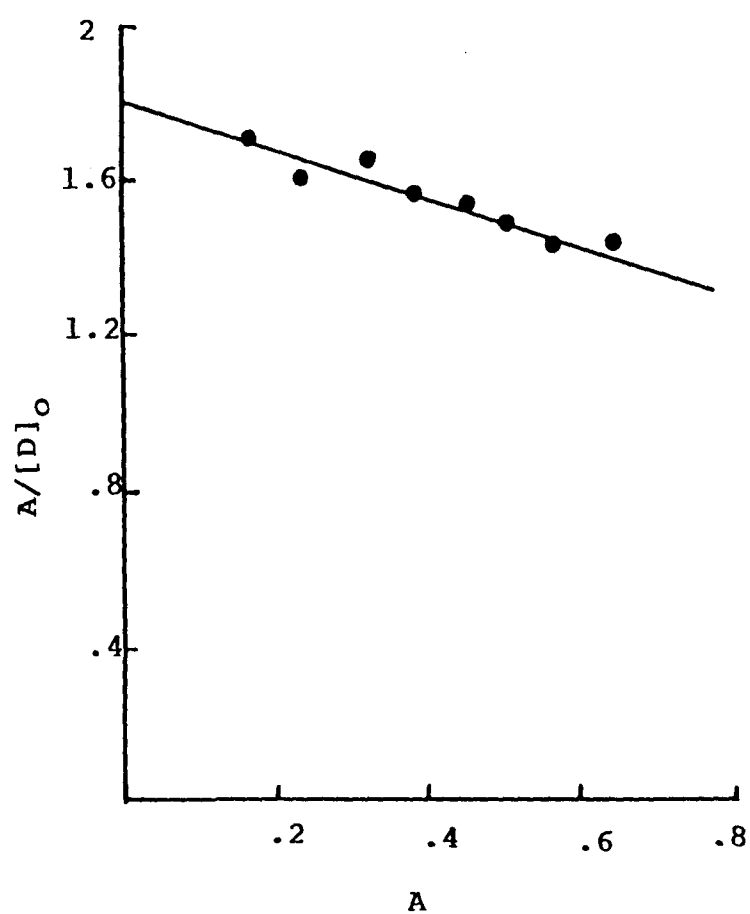


Fig. 2 The Foster plot for the 3,5-Dinitrobenzoic acid-Aniline system.

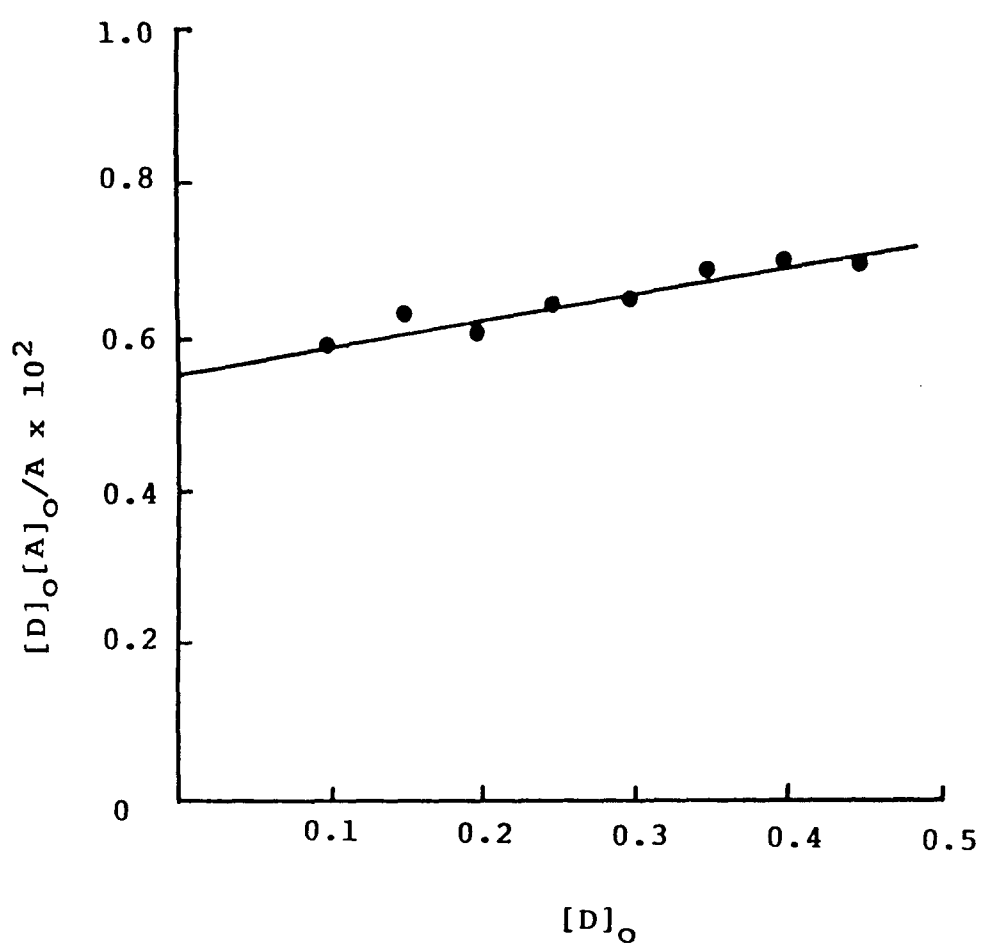


Fig. 3 The Scott plot for the 3,5-Dinitrobenzoic acid-Aniline system.

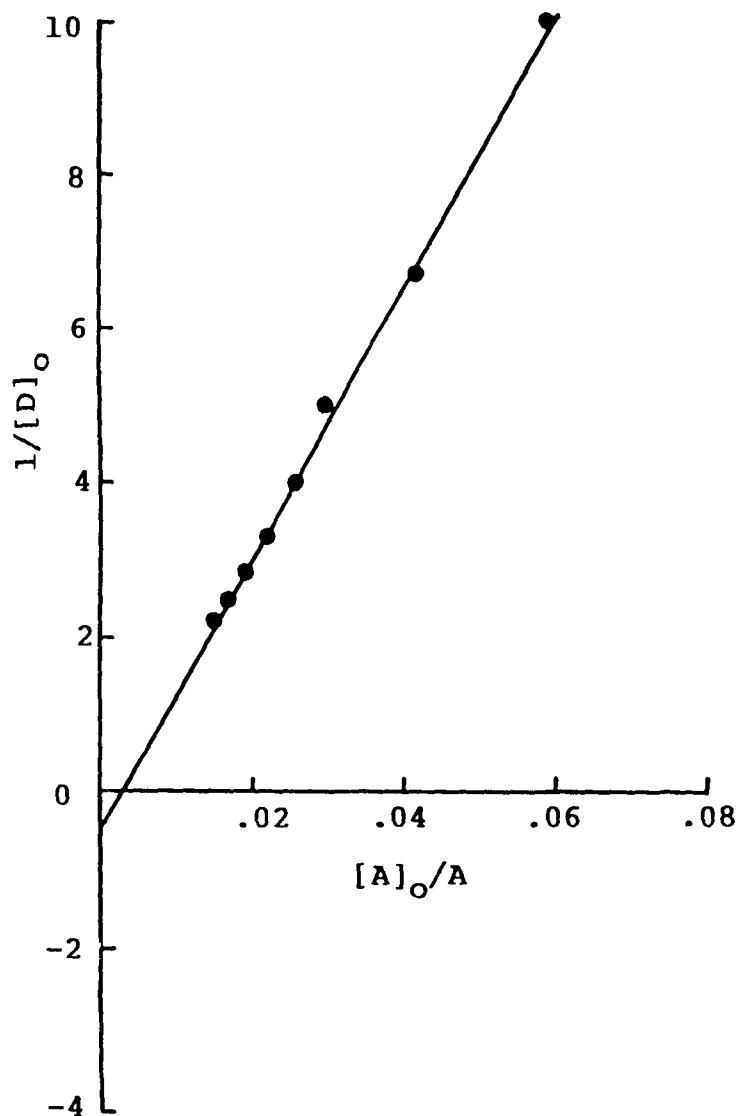


Fig. 4 The plot obtained by the New equation for the evaluation of the equilibrium constant of the 3,5-Dinitrobenzoic acid-Aniline system.

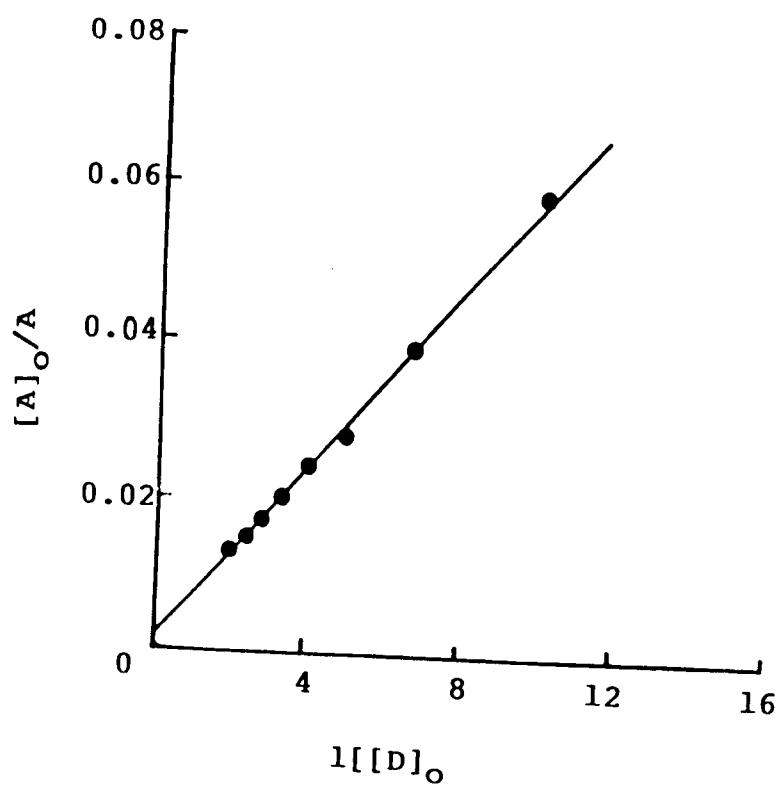


Fig.5 The Benesi-Hildebrand plot for the m-Dinitrobenzene-Aniline system.

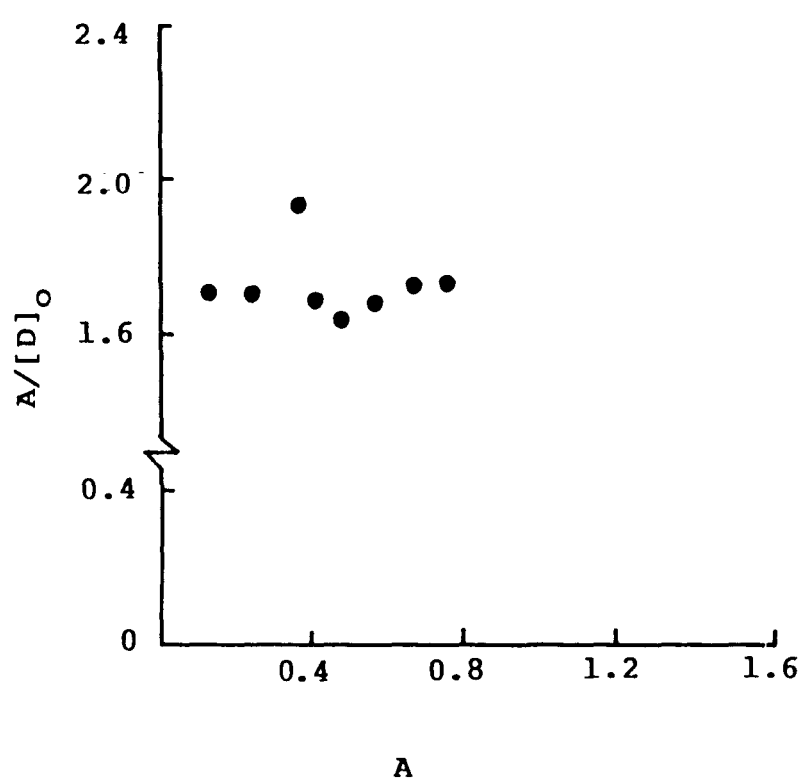


Fig. 6 The Foster plot for the m-Dinitrobenzene-Aniline system.

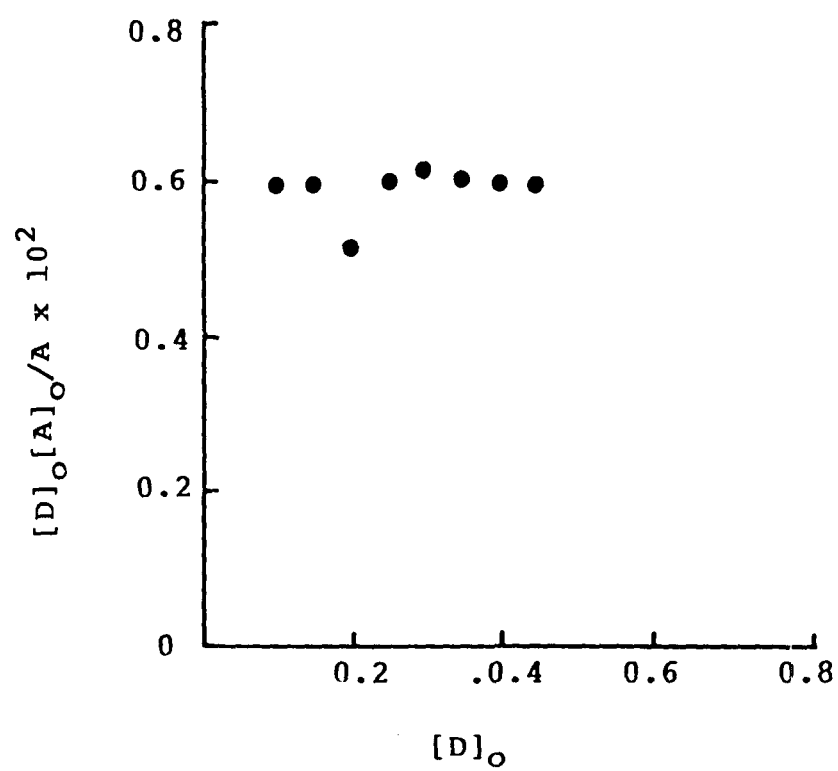


Fig. 7 The Scott plot for the m-Dinitrobenzene-Aniline system.

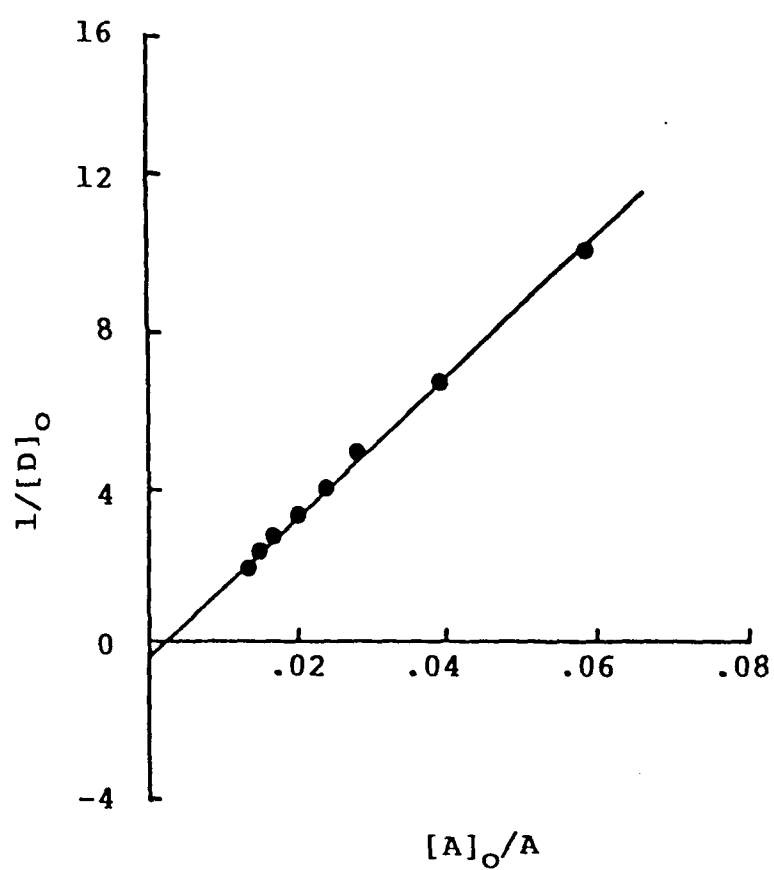


Fig. 8 The plot obtained by the New equation for the m-Dinitrobenzene-Aniline system.

TABLE - 1

ASSOCIATION CONSTANTS AND MOLAR ABSORPTIVITIES OF DINITROBENZENES-ANILINE COMPLEXES IN CCl_4
OBTAINED SPECTROPHOTOMETRICALLY BY USING DIFFERENT METHODS AT 303K

CT Complex	Donor	$K(\text{LM}^{-1})$			ϵ_{400}		
		Benesi-Hildebrand Method	Foster Method	Scott Method	New Method	Benesi-Hildebrand Method	Scott Method
3,5-Dinitrobenzoic acid	Aniline	.547	.660	.594	.471	322.5	303.3
* 1-Fluoro-2,4-dinitrobenzene	Aniline	5.667	N.O.	4.242	5.06	666.7	857.14
* 1-Chloro-2,4-dinitrobenzene	Aniline	.223	N.O.	N.O.	.128	917.4	N.O.
2,4-Dinitrotoluene	Aniline	.471	N.O.	N.O.	.361	250.0	N.O.
m-Dinitrobenzene	Aniline	.093	N.O.	N.O.	.131	1785.7	N.O.
						1335.9	

Calculation of ϵ_λ by Foster's Method has been omitted as it is rather involved.

* Since the solvent is non polar (CCl_4), in both these cases a molecular complex is expected over a π -complex.

N.O. = Not obeyed

small errors introduced will still lead to more reliable values. Table 1 gives the values of K and ϵ_λ obtained by using the new equation for the dinitrobenzenes - aniline complexes. These are compared with results obtained from other equations. Complementing table 1 figures 1 - 8 give representative trends. It is readily seen (Table 1) that the method of Foster and Scott failed for most of the complexes studied by me. In most cases the new equation gives lower values of K and higher values of ϵ_λ than the Benesi-Hildebrand equation. This is probably expected in light of the reasons outlined above. Moreover, ϵ_λ values obtained by the Benesi-Hildebrand eqn. are often so low that they may not even be the true values. The new equation can be an alternative to the Benesi-Hildebrand equation and it certainly does contain the unifying features of both Benesi-Hildebrand and Foster equations that K is measured without separation and that the separation of terms does not lead to K (Benesi-Hildebrand) but gives ϵ_λ leading to increased accuracy in both K and ϵ_λ .

Evaluation of Association constant by NMR spectrometry

The evaluation of K by NMR spectrometry is now being used extensively. The methods of evaluating K by NMR spectrometry use analogues of the equations used in electronic spectroscopy. The equations used are:

(1) Hanna-Ashbaugh Equation⁸ (an analogue of the Benesi-Hildebrand Equation) which takes the form:

$$\frac{1}{\Delta} = \frac{1}{K} \frac{1}{\Delta_o} \frac{1}{[D]_o} + \frac{1}{\Delta_o} \dots (6)$$

where Δ is the shift in frequency between 'free' and 'complexed' reactants, Δ_o is the shift in pure complex (not measurable), K is the association constant and $[D]_o$ is the initial concentration of donor, taken in large excess over the acceptor. The acceptor concentration is kept constant while the donor concentration varied and the shifts in frequency of an acceptor peak in the complex measured with respect to the free acceptor. A plot of $1/\Delta$ vs $1/[D]_o$ gives a straight line with $1/\Delta_o$ as intercept and $1/K \Delta_o$ as slope, whereby K and Δ_o can be evaluated.

(2) Foster-Fyfe Equation⁹ (an analogue of the Foster-Hammick-Wardley Equation). It is a rearranged form of Equation 6.

$$\frac{\Delta}{[D]_o} = -\Delta K + \Delta_o K \dots (7)$$

A plot of $\Delta/[D]_o$ vs Δ yields a straight line with a negative slope. The negative slope gives K directly.

(3) Qureshi-Varshney-Kamoonpuri Equation¹⁰ (an analogue of Scott equation). It takes the form:

$$\frac{[D]_0}{\Delta} = \frac{1}{K} - \frac{1}{\Delta_0} + \frac{[D]_0}{\Delta_0} \quad \dots (8)$$

A plot of $[D]_0/\Delta$ vs $[D]_0$ gives a straight line with slope equal to $1/\Delta_0$ and the intercept equal to $1/K\Delta_0$, whereby K and Δ_0 can be evaluated.

(4) I now propose a new equation which is a rearranged form of the equation 6. This is the NMR analogue of the new equation used in UV-visible spectroscopy earlier.

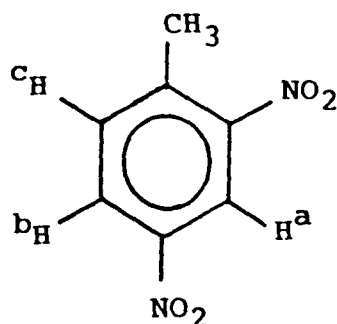
$$\frac{1}{[D]_0} = K \Delta_0 - \frac{1}{\Delta} - K \quad \dots (9)$$

A plot of $1/[D]_0$ vs $1/\Delta$ gives a straight line with the negative intercept giving K directly. Δ_0 can be evaluated from the slope.

To study the utility of the new equation (eqn. 9), the 2,4-Dinitrotoluene - Diphenylamine system was selected as it has been shown to be a well defined charge-transfer complex¹¹. This system has been again reinvestigated here by taking a much higher donor to acceptor ratio. All the NMR spectral data were recorded on varian 60D spectrometer working at 60 MHz.

In the charge-transfer complex in CCl_4 , there are upfield shifts of the acceptor (dinitrotoluene) protons. The maximum shift being for proton 'a' which is under the

electron withdrawing effect of the two neighbouring nitro groups.



Equilibrium constants were evaluated by all the four equations taking the three protons 'b', 'c' and '-CH₃' into consideration (Figures 9, 10, 11 & 12). Equilibrium constants are given in table 2. As expected NMR association constants vary with nuclei being measured¹². However, what was most unexpected is the fact that association constants measured by different methods are almost the same, a fact not borne by other workers. Usually different methods give different values of K. This aspect is common to K measured by electronic spectroscopy^{6,7,13} as well as NMR spectrometry¹⁰. Perhaps this is the first report where equal values of K are obtained by different methods. The results obtained show that the NMR analogue of the new equation proposed here satisfactorily reproduces the value of K obtained by other equations, showing the usefulness of the equation.

The inherent advantage of the new equation is, however, for the electronic spectroscopy viz that K can be

measured directly without recourse to separation of terms and gives satisfactory results even in cases where Foster and Scott equations are not obeyed. The first advantage also obtains for the NMR analogue of the new equation.

TABLE - 2

NMR ASSOCIATION CONSTANTS (K) AND PROTON SHIFTS FOR THE PURE COMPLEX RELATIVE TO THE ACCEPTOR (Δ_o) FOR COMPLEX OF DNT AND DPA IN CCl_4 AT 303K

Method	Nucleus considered					
	H(b)		H(c)		H(-CH ₃)	
	K(LM ⁻¹)	Δ_o	K(LM ⁻¹)	Δ_o	K(LM ⁻¹)	Δ_o
Hanna-Ashbaugh	.334	59.88	.076	95.24	.091	142.86
Foster-Fyfe	.333	-	.075	-	.087	-
Qureshi-Varshney Kamoonpuri	.342	59.03	.072	100.00	.095	118.11
New method	.345	58.14	.078	95.24	.096	90.91

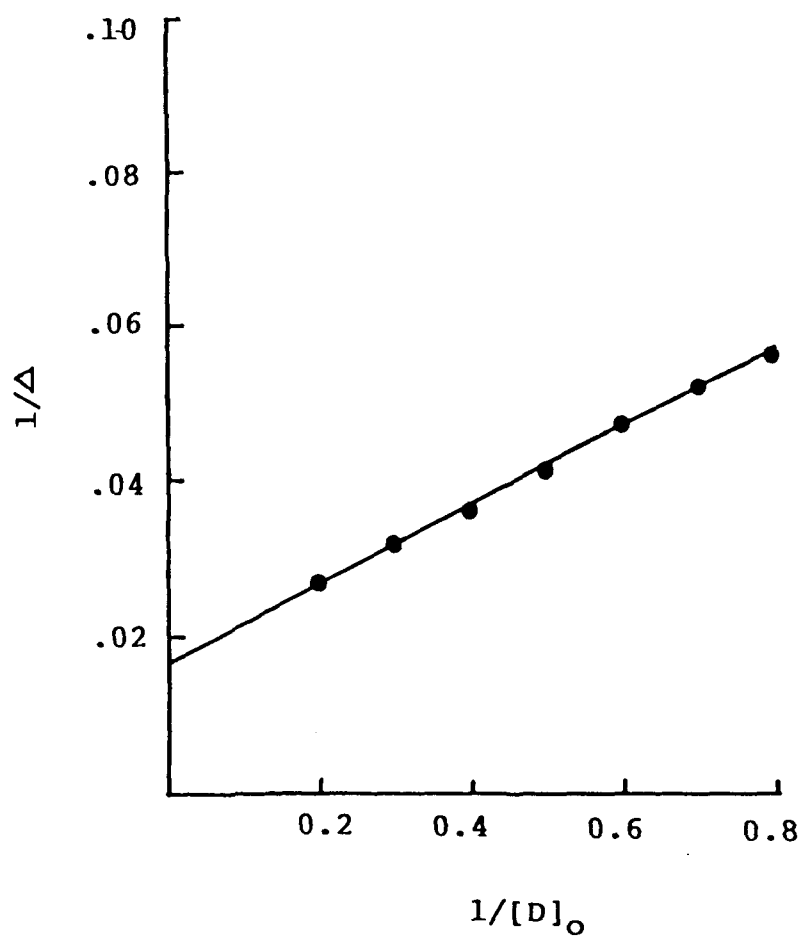


Fig. 9 The Hanna-Ashbaugh plot for the 'b' proton of Dinitrotoluene in the Dinitrotoluene - Diphenylamine system by the NMR method.

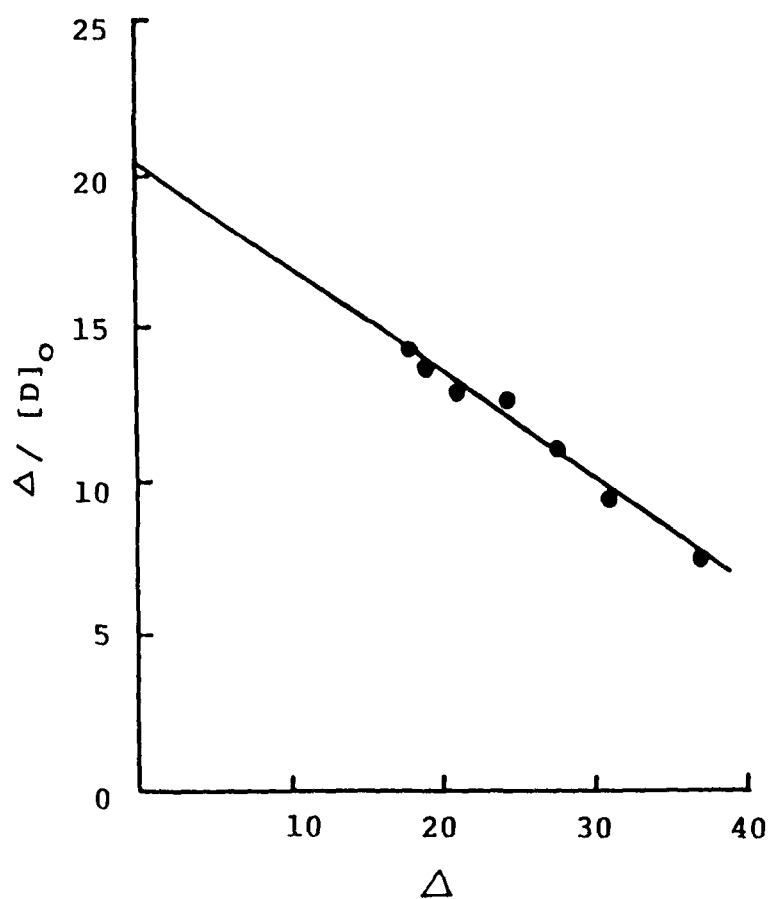


Fig. 10 The Foster-Fyfe plot for the 'b' proton of Dinitrotoluene in the Dinitrotoluene-diphenylamine system by the NMR method.

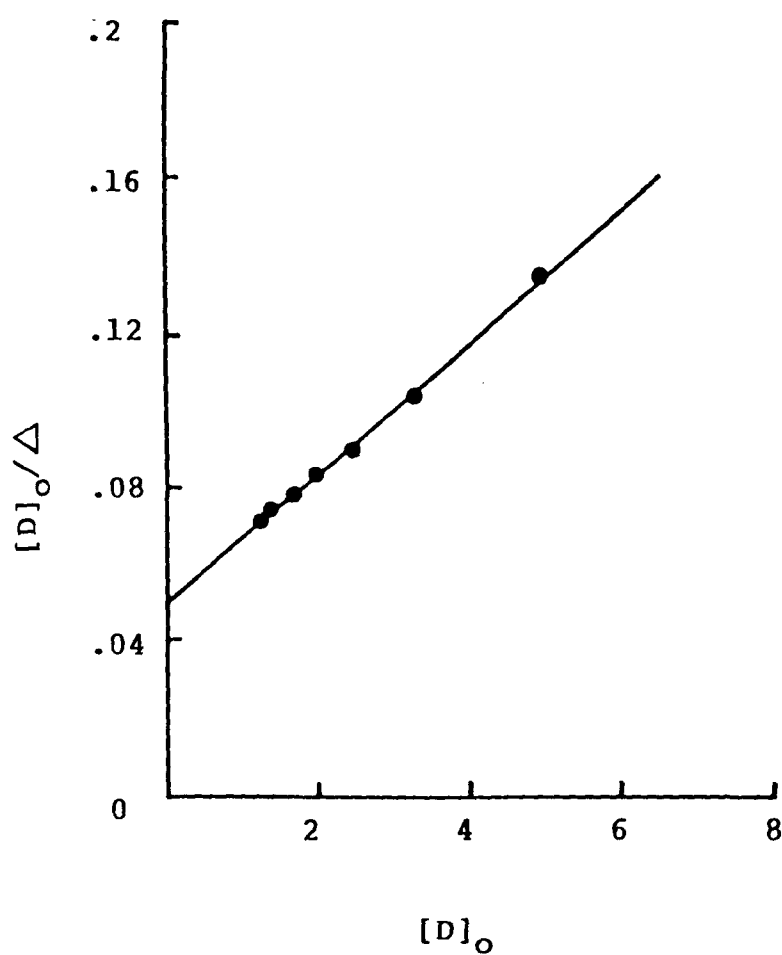


Fig. 11 The Qureshi-Varshney-Kamoonpuri plot for the 'b' proton of Dinitrotoluene in the Dinitrotoluene-Diphenylamine system by the NMR method.

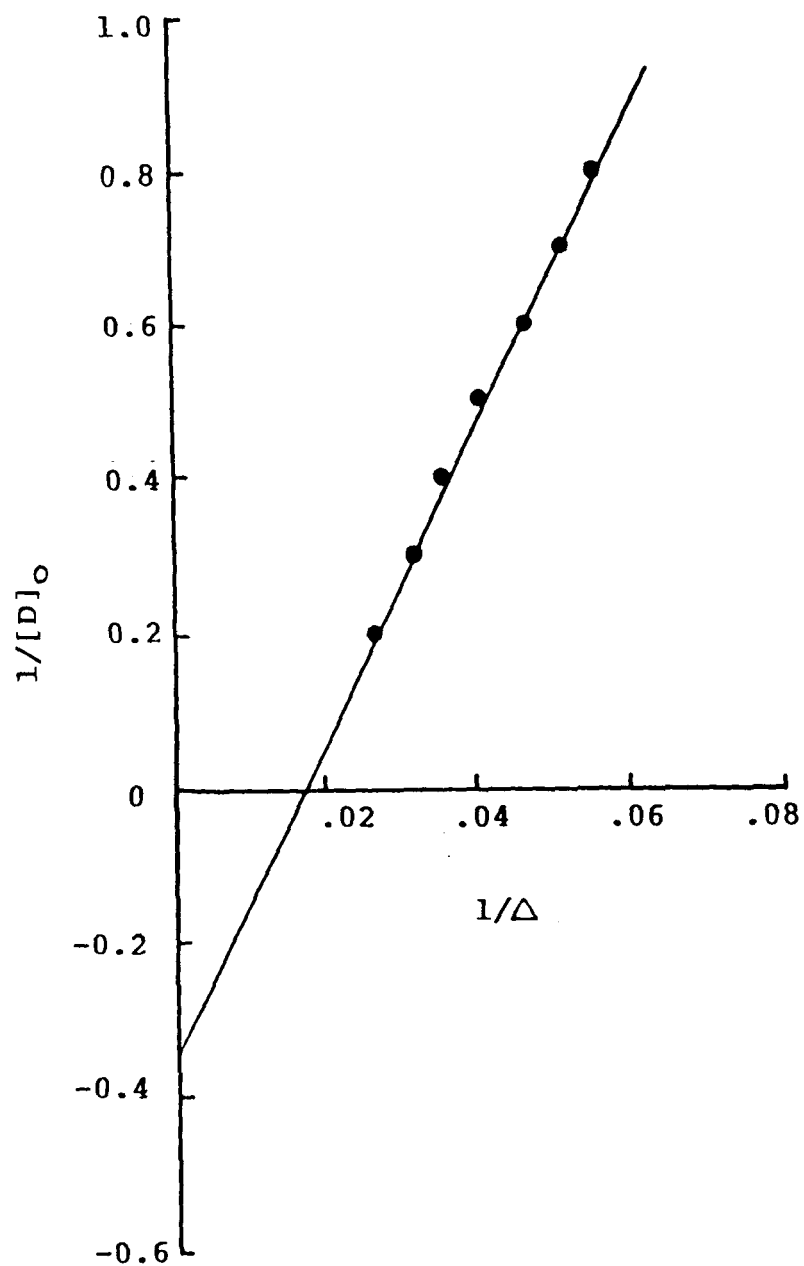


Fig. 12 The New plot for the 'b' proton of Dinitrotoluene-Diphenylamine system by the NMR method.

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CHAPTER - 7

A KINETIC METHOD OF ANALYSIS FOR AN IMPORTANT PHARMACEUTICAL 2,4-DINITRO- PHENYLHYDRAZINE

INTRODUCTION

2,4-Dinitrophenylhydrazine (DNPH) is an important reagent for a variety of functional groups and specially for the carbonyl group. However, it has an important role in various agricultural, biological and pharmaceutical applications. It is used in the determination of larvicidal activity¹. It is used in the preparation of herbicides². The effects of dicumarol were investigated in the Ames reversion test by assaying several mutagens including DNPH in the presence of a variety of metabolic systems where it was noted that dicumarol partially prevented metabolic loss of mutagenicity³. The structural basis of the mutagenicity of chemicals including DNPH has been studied in *Salmonella typhimurium*⁴. An ion-exchange method has been developed for the development of some chemical carcinogens and cancer suspect agents which include DNPH⁵. An improved bioluminescence test for mutagenic agents has been described. All the chemicals including DNPH which are active to the Ames test gave a positive response⁶. A model has been described for predicting mutagenicity of organic compounds like DNPH⁷. DNPH has been used for improving service life of engine oil⁸. The mechanism of hepatic megamitochondria formation by ammonia derivatives like DNPH has been studied⁹. HPLC has been used for the estimation of aldehydes in blood and tissues via the analysis of their DNPH adducts¹⁰. A comparison has been made for DNPH and correlation between

toxic potency in animals and toxic potency in *Salmonella typhimurium*¹¹. DNPH-uracil compound is an anticancer drug and its analysis was carried out in pure and dosage forms¹².

It is therefore evident that the analysis of DNPH is an important requirement. The general methods applied for the analysis of polynitroaromatics including DNPH suffer from the disadvantage that the colours formed are highly unstable. Therefore, a kinetic method would be ideal. Such a method is described below.

EXPERIMENTAL

2,4-Dinitrophenylhydrazine (DNPH) was E. Merck (G.R.); piperidine, BDH (Analar); DMSO, Baker Analysed Reagent and other amines were Analytical Reagent grade. The kinetics of the reaction was carried out spectrophotometrically on Bausch and Lomb spectronic-20 at 640 nm in a temperature controlled water-bath. The amine was kept in excess in all cases studied. The rate of decomposition of the coloured product was monitored with time.

RESULTS AND DISCUSSION

On mixing of solutions of 2,4-dinitrophenylhydrazine (DNPH) and aliphatic amines generate a deep green colour with a λ_{max} centred at 640 nm. Amine excess was maintained in all cases of the kinetic study. The kinetics of

decomposition of the green colour was studied at 640 nm. The loss in absorbance was measured as a function of time. However, before reporting the kinetic results we would like to reflect on the interferences. As has been mentioned a deep green colour is formed, therefore interference is expected from those compounds that give a colour (notably green colour) under identical reaction conditions. Absolutely no colours are observed with Carbohydrates (L(+)-arabinose, lactose, D(+) melezitose, glucose, rhamnose, sucrose); acids (acetic, formic, tartaric, phthalic, pyrogalllic, oxalic); alcohols (propan-2-ol, ethyl, methyl, 2-methylpropan-2-ol, amyl, isoamyl); heterocyclic bases (pyridine); aldehydes (formaldehyde, acetaldehyde, benzaldehyde, paraldehyde, p-chlorobenzaldehyde); ketones (acetophenone, cyclopentanone, cyclohexanone, propiophenone, benzophenone); hydrocarbons and their derivatives (benzene, xylene, o-dichlorobenzene, brombenzene, toluene); ethers (diethyl, anisole, 1,4-dioxan); amino-acids (DL-tryptophan, L-lysine, DL-phenylalanine, L-histidine); anilides (acetanilide, benzanilide); nitriles (aceto, benzo); amides (acetamide, benzamide); phenols (phenol, m-cresol, resorcinol); miscellaneous (chloroform, carbon tetrachloride, urea, thiourea).

In the kinetic studies ammonia, diethylamine, ethanolamine and n-butyl amine all gave first order plots.

Only piperidine gave second order plot (Figure 1 for example). This shows that the decomposition is second order in DNPH. It is rather difficult to obtain rate constants as it is not possible to get a stable complex under the reaction conditions studied. However, apparent rate constants viz slopes of plots of $\frac{1}{A}$ vs t may be reported.

Since the system is complex and since true rate constants are not being measured there is no apparent trend in the various k_{app} values; however, the reproducibility (as seen from table 1) is satisfactory.

The decomposition is faster at elevated temperatures and effect of temperature is shown in Figure 2. Piperidine can be distinguished from other aliphatic amines like ammonia, diethylamine, ethanolamine and n-butylamine as all of these give clean first order plots while in second and third order plots there is a curvilinear dependence. Piperidine shows a curvilinear dependence in the case of first and third order plots. Piperidine, however, cannot be determined in the presence of these amines as all give an identical colour and all finally decompose to products.

The product of decomposition of DNPH and ammonia has been shown to be 6-nitro-1-hydroxy-1,2,3-benzotriazole¹³ by probably a very complex mechanism. Piperidine is also expected to form triazoles, however, we are mainly interested

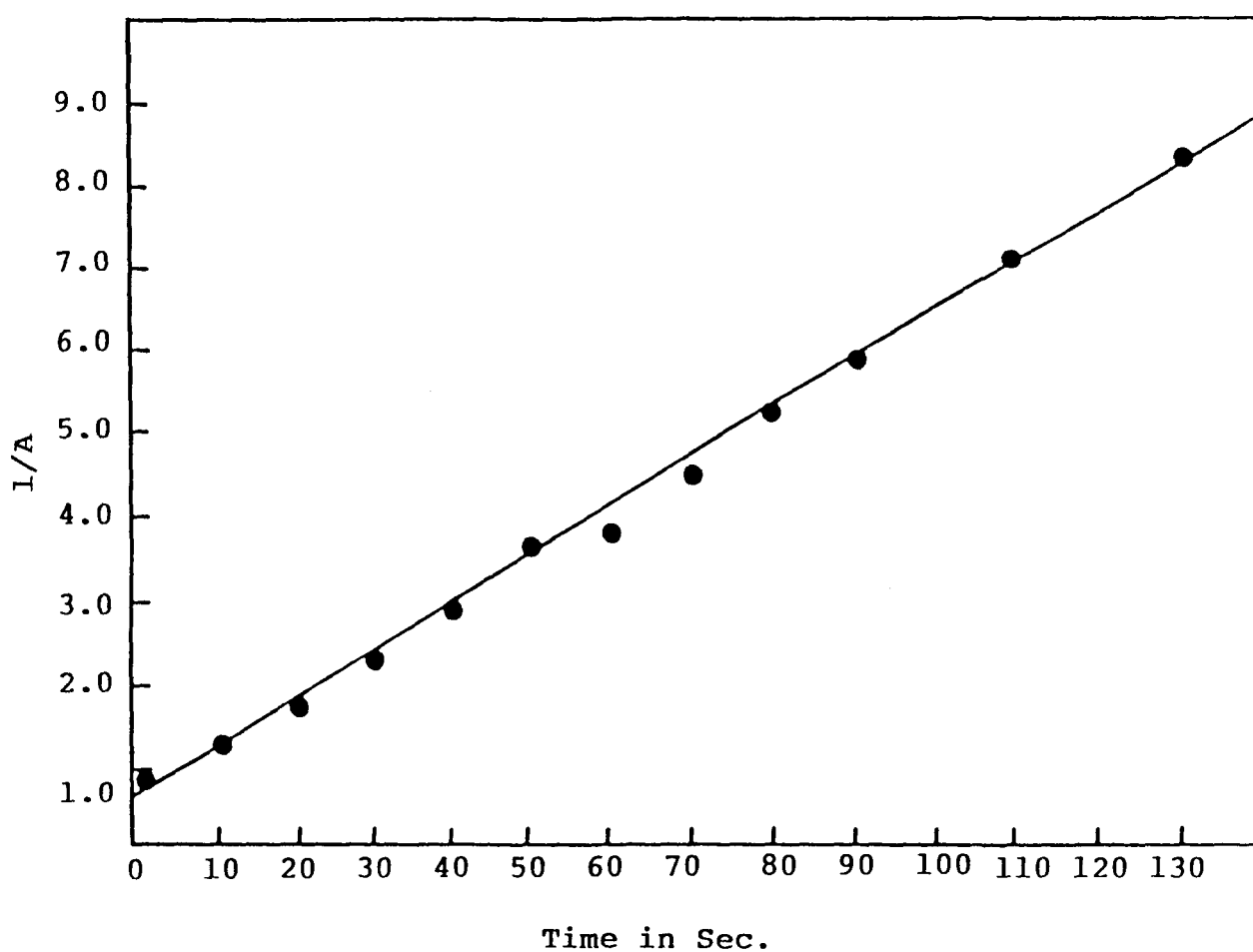


Fig. 1 Kinetic run for the reaction of 10×10^{-4} M DNPH with piperidine in dimethylsulfoxide at room temperature (278°K).

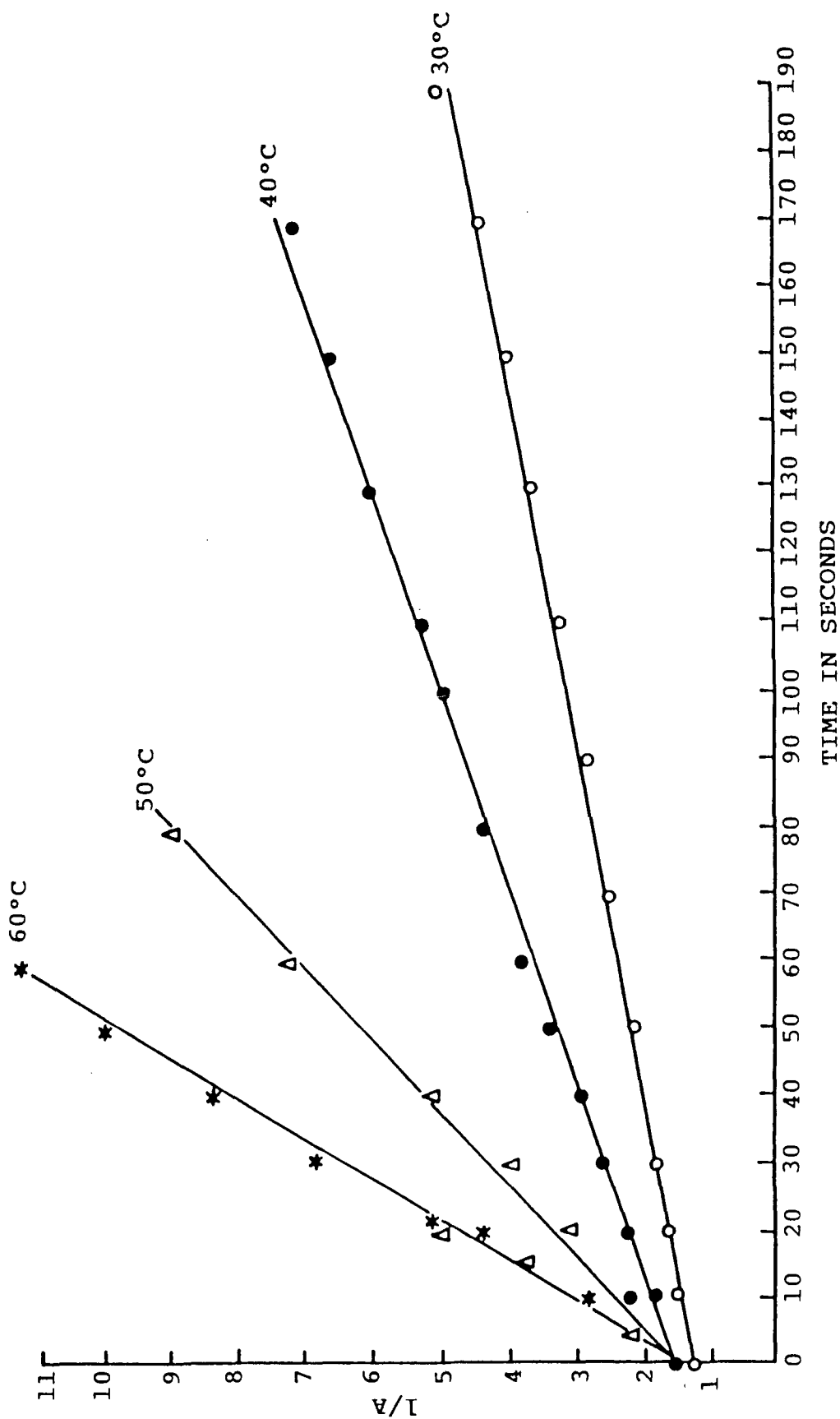


Fig. 2 Temperature dependence of the DNPH - piperidine coloured complex. DNPH 4×10^{-4} M:
piperidine 5×10^{-3} M.

TABLE 1

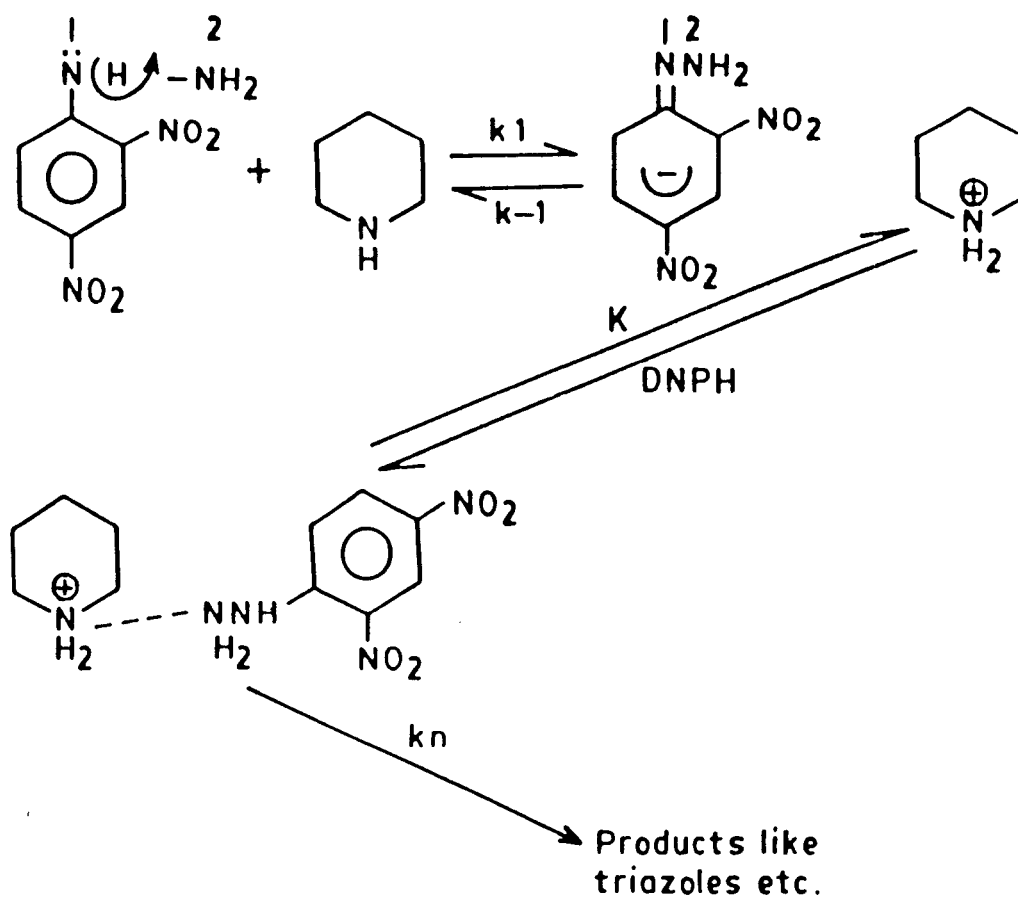
k_{app} values for individual runs	
<hr/>	
Concentration of DNPH	k_{app} for two individual runs
3×10^{-4} M DNPH	1. 1.1×10^{-3}
	2. 1.11×10^{-3}
5×10^{-4} M DNPH	1. 1.45×10^{-3}
	2. 1.38×10^{-3}
7×10^{-4} M DNPH	1. 0.83×10^{-3}
	2. 0.74×10^{-3}
10×10^{-4} M DNPH	1. 0.98×10^{-3}
	2. 1.0×10^{-3}

in the coloured product. Since the reaction is second order in DNPH one may assume even in this complex system that two molecules of DNPH associate with one molecule of piperidine. It has been previously proposed^{14,15} that aliphatic amines react with DNPH by a proton loss mechanism as in the case of dinitroaniline derivatives¹⁶. Based on analogous reasoning we may postulate the mechanism given in Scheme 1.

There are many reactions where charge-transfer complexes are involved. The σ -complexes formed by the interaction of polynitroaromatics and aliphatic amines are expected to include a charge-transfer complex somewhere on the reaction profile¹⁷. I propose that in the above mechanism, the σ -complex formed plays an important role along with the hydrogen bonded complex between dinitrophenylhydrazine and protonated piperidine molecules. It is expected that charge-transfer contributes extensively to the hydrogen bond. Such an interpretation can be understood in the light of new concepts that most hydrogen bonded systems have significant contribution from charge-transfer forces¹⁸. The overall reaction, therefore, is a case of a reaction in which molecular association is involved.

k_n signifies a combined rate constant for the formation of the final products which may be formed by different pathways.

The method can be used in the range 0-120 ppm of DNPH. This is a relatively narrow range probably because at



SCHEME I

higher DNPH concentrations the absorbance goes much beyond the limit of photometric accuracy. The calibration curve (Figure 3) has however been plotted in terms of Moles Liter⁻¹. The two are easily convertible.

The reaction of other aliphatic amines is typified by the case of ammonia, where clean first order kinetics is followed (Figure 4). A plot of $1/\text{Intercept}$ vs concentration of DNPH gives a curve. The rate constants however are linearly related to concentration (figure 5) and may provide a complementary method for the determination of DNPH.

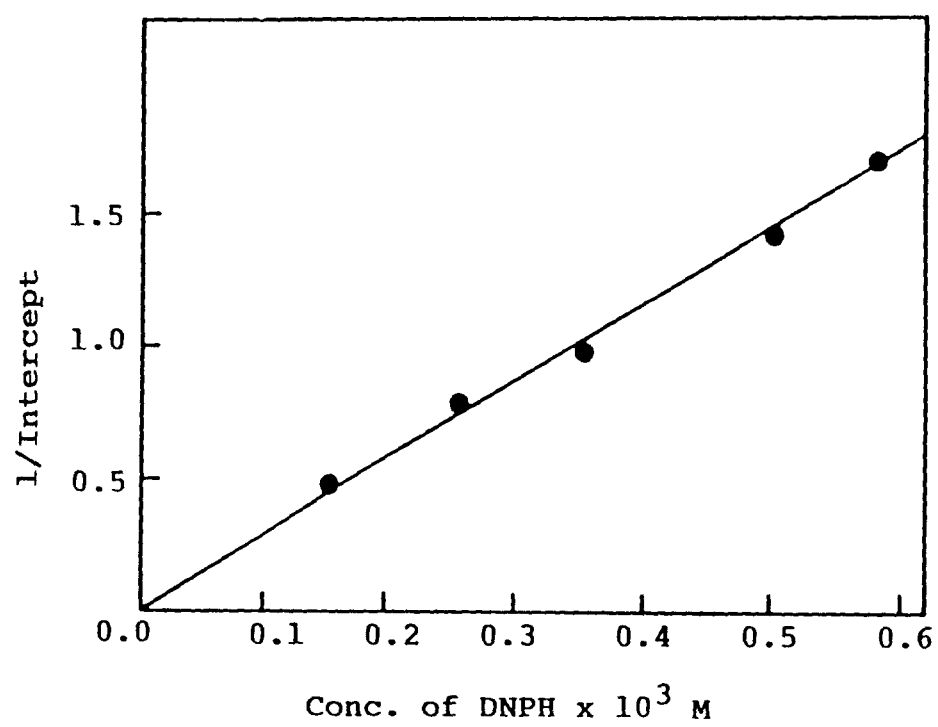


Fig. 3 Calibration plot for DNPH.

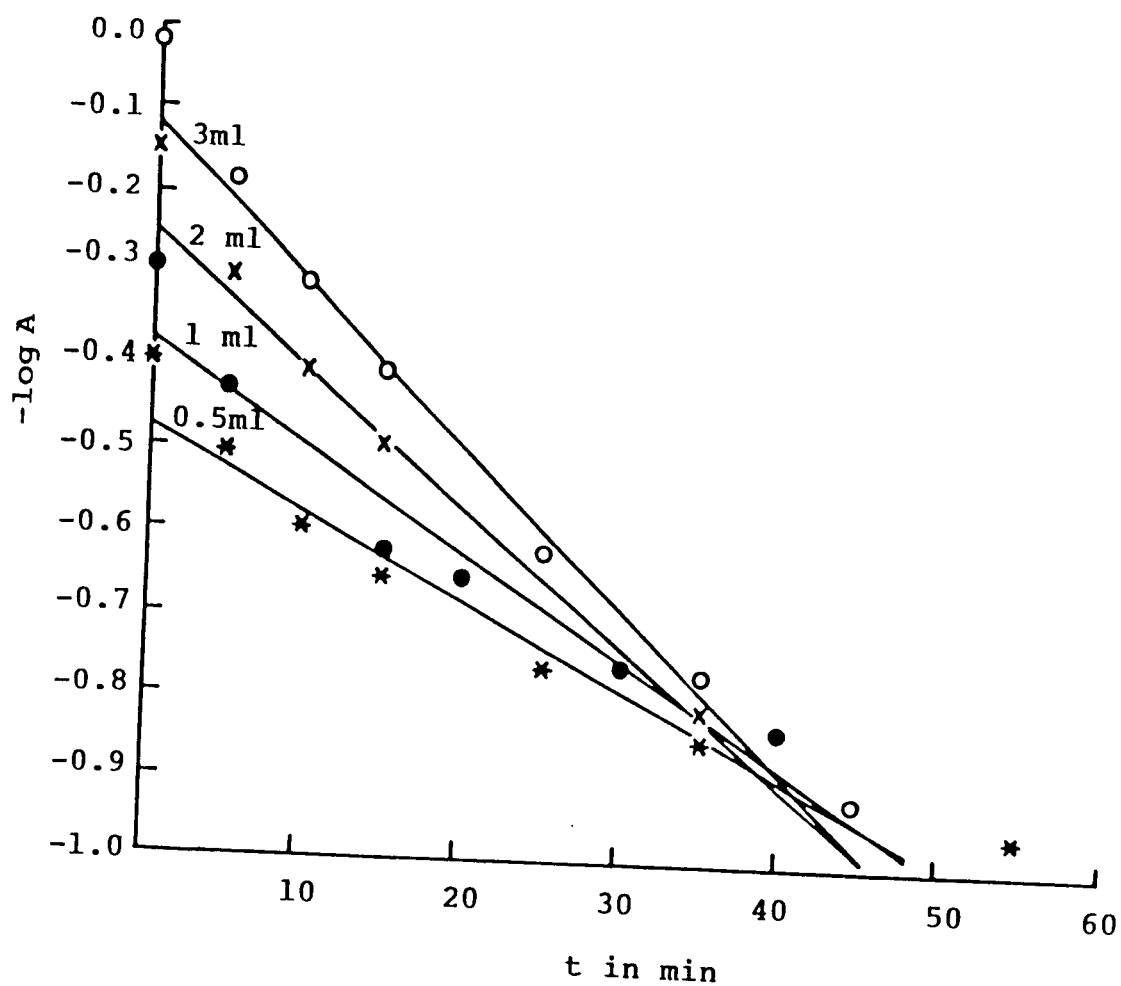


Fig. 4 First order plots for the Ammonia-DNPH system.

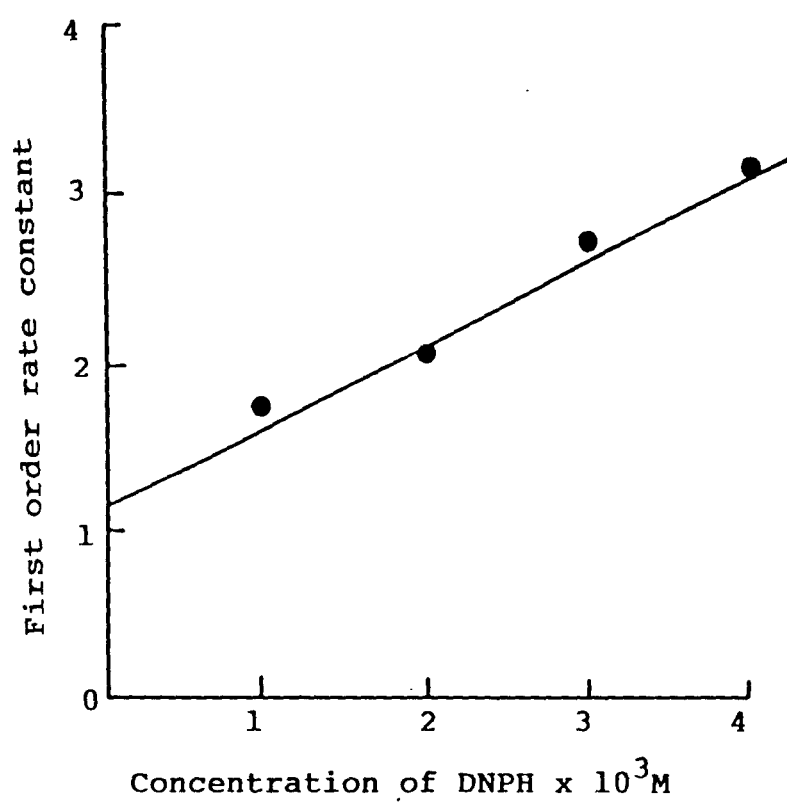


Fig. 5 Relation of rate constants for the DNPH-Ammonia reaction as a function of DNPH reaction.

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